JOURNAL

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THE CHEMICAL SOCIETY.

TRANSACTIONS.

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I.—*The Preparation of Ethyl Bromide.*

By Alfred Holt.

In a recent paper (T., 1915, **107**, 1489) F. E. Weston discusses the best conditions for the preparation of ethyl bromide. As the present author has recently had occasion to prepare this compound on a fairly large scale, and, as Mr. Weston truly remarks, its preparation has assumed great importance, the following notes are possibly worth recording.

The problem presented was how to prepare the greatest quantity of ethyl bromide from any given weight of sodium or potassium bromides, for, owing to the high price of bromides compared with alcohol or sulphuric acid, a moderate waste of the latter substances was immaterial.

The great difficulty to contend with was the production of ether, since its separation from ethyl bromide by means of concentrated sulphuric acid and subsequent washing until free from acid is both tedious and wasteful.

The usual mixture was prepared as follows: To 1500 c.c. of concentrated sulphuric acid were gradually added 900 c.c. of water, and, after cooling, 1500 c.c. of absolute alcohol were slowly run in, care being taken to prevent the temperature rising too much. When cold, 1100 to 1200 grams of potassium bromide or an equivalent quantity of the sodium salt were added. [When sodium bromide ($NaBr,2H_2O$) was employed the volume of water added

to the acid was slightly diminished]. The whole mixture was then heated in a 14-litre flask on a sand-bath at the lowest temperature at which ethyl bromide would distil over. The distillation required about eight or nine hours.

The ethyl bromide was collected in water, washed by repeated shaking with water, and dried over calcium chloride.

Determination of the boiling point in order to test the purity of the compound is unsatisfactory, as a mixture of ether and ethyl bromide of constant boiling point can be obtained, so the purity of the product was determined by its specific gravity. Usually the ethyl bromide was practically free from ether.

The best yield obtained was 96 per cent. calculated on the weight of anhydrous bromide taken, and it rarely fell below 90 per cent., the variations undoubtedly arising from irregularities in the temperature at which the distillation was carried out.

Practically no hydrobromic acid distilled over.

The largest amount of reaction mixture employed in any single preparation was about 8000 grams, and the distillation, although tedious, presented no difficulties.

It is clear from both the preparations of Mr. Weston and the present author that low temperature with consequent slow distillation and a large quantity of a not too concentrated alcohol-sulphuric acid-water mixture are necessary for good yields.

Frothing never gave the least trouble.

THE UNIVERSITY,
LIVERPOOL.

[*Received, November 23rd*, 1915.]

II.—*The Rate of Growth of Bacteria.*

By ARTHUR SLATOR.

CHEMICAL reactions brought about by micro-organisms usually proceed under conditions where development of the organism and changes in the composition of the nutrient medium take place simultaneously. In a study of the dynamics of such reactions the rate of development of the micro-organism is of fundamental importance.

The rate of growth of bacteria has received a considerable amount of attention (Lane-Claypon, *J. Hygiene*, 1909, **9**, 239; Penfold and Norris, *ibid.*, 1913, **12**, 527; and others).

The usual method of investigation is to allow small seedings of bacteria to grow in a suitable medium under definite conditions,

and to estimate the number after given intervals of time by the well-known method of "plating." It has been shown for many growths of bacteria that if the development takes place unrestrictedly the logarithmic law of increase holds good. If care is taken to prevent any change in the nutrient medium in which the bacteria are growing, the bacteria can apparently develop indefinitely, always multiplying at the same rate. This can be experimentally realised by making repeatedly sub-cultures in the early stages of growth. If the bacteria are allowed to develop without such precautions, the medium changes in composition, and owing either to lack of necessary food or to the production of poisons the rate of growth of the bacteria diminishes, and they finally cease to increase. Another phase of bacterial growth has been observed and thoroughly examined by Penfold and by Ledingham and Penfold (*J. Hygiene*, 1914, **14**, 215). This is the period of bacterial lag which takes place before the bacteria develop at the constant maximum rate. Bacterial lag is invariably observed when old cultures are seeded into a fresh nutrient medium.

In an investigation on the rate of fermentation by yeast cells growing in lightly hopped wort it has been shown that rates of growth can be determined in other ways (Slator, *Bio-Chem. J.*, 1913, **7**, 197). During the period of unrestricted growth the constant of growth is given by the equation $0{\cdot}434\,k = \frac{1}{t}\log\frac{N+n}{N}$, where the number of yeast cells increases from N to $N+n$ in the time t. The value of k can also be obtained by measuring the rate of fermentation over this period of growth. The amount of fermentation is proportional to the number of yeast cells which have developed, and the rate of fermentation is given by the equation

$$0{\cdot}434\,k = \frac{1}{t}\log\frac{S+s}{S}.$$

where S is the amount of sugar fermented when the yeast cells grow from a very small seeding to N, and $S+s$ the amount when the growth has reached $N+n$. The values of k determined by the two methods showed good agreement.

Attempts have now been made to estimate the rate of growth of bacteria by methods which do not involve the trouble of "plating."

The micro-organism chosen for the experiments was an organism producing lactic acid and occurring in malt-wort. If a sample of wort with its natural infection is kept at a temperature of 45—50° for a short time these organisms alone develop, for the temperature is too high to admit of the growth of others. In the technical production of lactic acid these bacilli are of considerable value,

and have been very thoroughly studied (see "Gärungsbakteriologisches Praktikum," W. Henneberg, Berlin, 1909, 445—462).

A pure culture of the organism was isolated, and attempts were made to measure the rate of growth in malt-wort. Experiments were first made in order to ascertain if the constant of growth could be determined by measurements of the rate of production of lactic acid. Satisfactory results were not obtained, for it was found that even small quantities of acid diminish the rate of development of the bacilli, and that the growth of the organism becomes retarded before sufficiently accurate titrations of the acid can be obtained.

Another method, however, gave good results. The bacterial content of the medium was determined by the following method. Wort in which the bacilli have developed in sufficient amount to cause turbidity shows on agitation a characteristic "silky" appearance. If finely divided asbestos is shaken with water a similar "silky" appearance is noticed. In each case the "silkiness" is caused by the thread-like form of the body causing the turbidity. It is possible to match the turbidity of an aqueous suspension of asbestos with one of the bacilli suspended in the medium in which it is growing. By preparing a number of standard asbestos tubes the relative concentration of bacilli in a liquid can be estimated by comparison with the standard tubes. These tubes contained asbestos in the ratio of amounts $1:\sqrt{2}:2:2\sqrt{2}:4$ with the quantity in the first standard adjusted so that the turbidity was just visible. With this method of determining bacterial amounts rates of growth can easily be measured. As an example, the measurement of the rate of growth at 45° of these bacilli can be given.

An active growth of the bacilli was obtained by growing the organism in test-tubes of wort (D 1·040) kept at 45°, and re-inoculating into fresh wort as soon as the growth became visible. It was found convenient to seal up the test-tubes, and as at the beginning of the experiments it was thought that air retarded the growth of the organism, all the tubes were exhausted before sealing. This precaution was subsequently found not to be necessary. When an active growth was obtained it was matched against one of the standards and then diluted with fresh wort to dilutions varying between 1/100th and 1/100,000th of the original concentration. The tubes were then sealed up and placed in a thermostat at 45°. The time required for the bacilli in the different tubes to develop to an amount measurable by one of the standards was observed. From the time (t) and the increase ($N+n/N$) the value of k is easily calculated. The following result was obtained:

TABLE I.

t hours.	$\frac{N+n}{N}$	$0{\cdot}434\,k$
2·53	119	0·82
3·48	800	0·83
4·00	2,260	0·84
4·73	9,060	0·84
5·02	18,100	0·85
		0·84

Generation time $=\frac{\log 2}{0{\cdot}84}=0{\cdot}358$ hour $=21{\cdot}5$ minutes.

The method of measuring bacterial amounts is only moderately accurate, but satisfactory values of k are obtained if the increase is large. Lower values of k, which increased during the time of the experiment, were obtained when the seeding was not grown several times at 45° before the measurements were made.

The Influence of Temperature on the Rate of Growth.

It was found that consistent values of k were obtained at other temperatures if the organism was first grown several times at the given temperature before the measurements were carried out. If this precaution was not taken, lower and variable values of k were obtained. Thus the organism grows at a rate 0·184 at 30° if the organism is seeded from a growth developing at 30°, but if seeded from one growing at 45° values increasing from 0·110 to 0·150 were obtained.

The measurements were carried out over the whole range of temperatures at which it is possible for the organism to grow. At lower temperatures the experiments were made under strictly sterile conditions; at higher ones this care is not necessary. The results are given in the following table:

TABLE II.

Temperature.	t	$\frac{N+n}{N}$		$0{\cdot}434\,k$.	$0{\cdot}434\,k$ from repeat experiments.
58·0°	No growth.				
55·0	Slight growth.				
52·5	5·5	614		0·51	
	6·5	5,220		0·57	
	10·3	317,000		0·54	
			Mean	0·54	
50·0	3·1	614		0·90	
	3·9	5,220		0·95	
	4·2	31,500		1·07	
	5·4	270,000		1·01	
			Mean	0·98	1·04
45·0	See Table 1.		Mean	0·84	0·080—0·090

TABLE II (*continued*).

Temperature.	t.	$\frac{N+n}{N}$		0·434 k.	0·434 k from repeat experiments.
40·0	4·0	305		0·62	
	5·25	1,550		0·61	
	6·0	5,530		0·62	
	6·8	23,400		0·64	
			Mean	0·62	
35·0	6·5	195		0·35	
	8·5	830		0·345	
	9·6	4,180		0·38	
	11·6	29,800		0·385	
			Mean	0·365	
30·0	18·0	1,840		0·181	
	21·0	7,800		0·185	
	25·0	46,80)		0·187	
			Mean	0·184	
25·0	29·0	277		0·084	
	43·0	3,310		0·082	
	49·5	19,900		0·087	
			Mean	0·084	0·081
22·0	90·0	126		0·02	
20·0	No growth				

It will be seen from these figures and from the accompanying curve that the influence of temperature on the rate of growth is very great. At 20° no growth takes place; at 22° slow growth; and at 25°, $0{\cdot}434k = 0{\cdot}083$. The value of k increases steadily up to a temperature of about 50°, when the maximum rate of growth occurs. At 52·5° the rate is nearly halved, although it is interesting to note that consistent values were obtained. At 55° the growth is slight, and soon stops; at 58° no growth takes place.

The temperature-quotient of the rate of growth varies, therefore, between a very large value at about 20° to a value of 1 at about 50°; it then becomes less than 1, and finally zero.

There is little advantage to be gained by giving these quotients, for no doubt the reactions which have a controlling influence on the rate of growth at one given temperature are different from what they are at another temperature, and the figures, therefore, cannot be considered true temperature-coefficients.

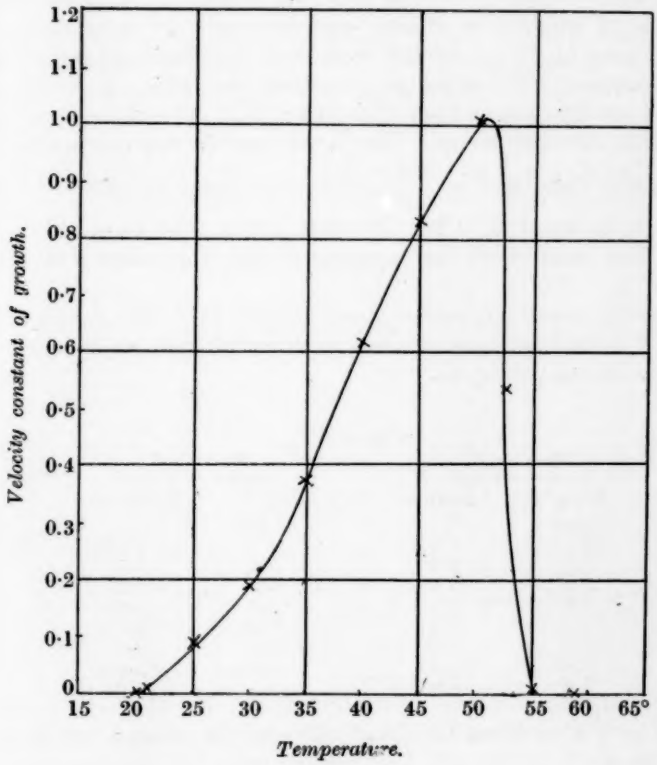
The Influence of Lactic Acid on the Rate of Growth.

If the bacilli are allowed to grow indefinitely in wort having D 1·040, the production of lactic acid is about 100° (1° equals an

increase of $N/1000$-acid). The main part of the acid is produced when the development is greatly retarded, for even 5·6° acid is sufficient to lower the rate to 0·55 and 11·1° to 0·35.

It was thought possible that if the bacilli were grown several times in an acid medium, such a growth would be less influenced by acid than the normal bacilli. The following table, however,

FIG. 1.



shows that this is not the case, for the values of k for normal bacilli and those for bacilli grown five times in wort to which 5° lactic acid had been added are almost identical.

TABLE III.

Temperature 45°. Addition of acid.	Normal bacilli.	"Acclimatised" bacilli.
0°	0·434 k=0·82	0·434 k=0·76
5·6	0·55	0·53
11·1	0·35 (decreasing).	0·29 (decreasing).

A Titration Method of Measuring the Rate of Growth.

Although the constant of unrestricted growth of the bacilli cannot be determined by direct measurement of the rate of production of acid, the value can be determined indirectly (see Slator, *Bio-Chem. J.*, 1913, **7**, 200). The method is best explained by an example.

Two quantities of wort were seeded with actively growing bacilli in a measured ratio (300:1 in this experiment), and kept at 45°. The rate of production of acid was measured by titration from time to time of 25 c.c. of the wort with $N/10$-sodium hydroxide, using sensitive litmus paper as an outside indicator. It was found that the one reaction preceded the other by a definite time, averaging in this case 2·88 hours. This is the time for the one seeding to grow to the other, that is, $\frac{N+n}{N}=300$ in a time 2·88 hours; $0{\cdot}434k$, therefore, is equal to 0·86. Another experiment gave the value 0·89. This result is in fair agreement with the value 0·84 given in table I.

Details of the titrations are given in table IV. The curves given in Fig. 2 show differences of times at three different stages, 2·9, 2·9, and 2·85 hours, averaging 2·88.

TABLE IV.

Seeding 1.		Seeding 2.	
Time. hours.	Titration.	Time. hours.	Titration.
0	1 c.c.	0	1 c.c.
1·0	1·0	5·2	1·0
3·0	2·0	6·0	2·2
3·5	3·2	6·5	3·0
5·0	4·7	7·2	4·2
5·2	5·0	7·5	4·5
5·8	5·3	8·0	4·8
6·8	6·0	8·5	5·5

Average difference of time read off from the curves = 2·88 hours.

$$0{\cdot}434\,k = \log\frac{300}{2{\cdot}88} = 0{\cdot}86.$$

Another experiment gave 0·89.

Influence of the Concentration of the Wort.

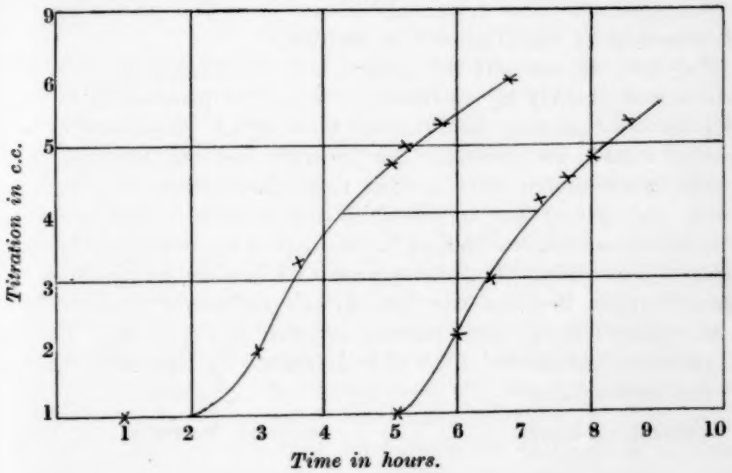
The rates of growth of the bacilli in worts having D varying between 1·060 and 1·008 were found to be the same; the rate of growth is therefore independent of the concentration of the wort over a large range. There is no doubt that in the case of even the dilute wort there is food diffusing to the cells sufficient to

maintain the maximum rate of growth, for otherwise the rate would be dependent on the concentration of the medium.

Penfield and Norris have shown in the case of *B. typhosus* that if the peptone solution in which the bacteria are growing is diluted sufficiently, the rate of growth is diminished, and that below 0·2 per cent. the time of generation is inversely proportional to the concentration of the peptone. In this case it is possible that diffusion of the food to the cell plays a controlling part in determining the rate of growth of the bacteria.

Slator and Sand (T., 1910, **97**, 922) have made a calculation of the limiting conditions under which diffusion alone would just supply yeast cells efficiently with sugar to enable them to exert their maximum fermentative activity. It was found that a concentra-

FIG. 2.



tion of the order of 1 milligram per litre was sufficient for the purpose if the enzyme were evenly distributed throughout the cell. If the enzyme were concentrated in a few points in the cell more concentrated solutions would be necessary.

Judging from these calculations, very dilute solutions would be efficient in supplying a micro-organism of the size of a bacterium with food for growth if the chemical reactions determining the rate of growth take place throughout the whole cell. If such reactions, however, take place in a small part of the interior of the cell more concentrated solutions would be necessary.

Whether or not diffusion plays a controlling part in the case investigated by Penfield and Norris could probably be determined by measurements of the temperature-coefficient, for the influence of

temperature on diffusion is much less than on growth measured under conditions of large food supplies.

Summary.

It is pointed out that the rate of development of micro-organisms is an important factor in the study of the dynamics of chemical reactions brought about by such organisms.

A convenient and accurate method of estimating rates of growth of bacilli is described. The method is applicable to bacilli which give a "silky" turbidity in the medium in which they grow. Such a turbidity can be matched against a standard one of asbestos suspended in water.

As an example, the rate of growth of an organism of the *B. delbrücki* type growing in malt-wort has been measured.

Measurements have been carried out over the whole range of temperatures at which growth is possible.

The rate of unrestricted growth of the organism cannot be determined directly by measuring the rate of production of lactic acid by the growing bacilli, for even small quantities of acid greatly retard the growth. An indirect method, however, gives results in agreement with the one mentioned above. The measurements are carried out in the following manner. Two quantities of wort are seeded, the seeding in one case being considerably larger than in the other. The development of acidity in the first case occurs earlier than in the second, the difference in time being that required for the one seeding to grow to the other. The rate of growth is calculated from this difference in time and the ratio of the seedings.

BURTON-ON-TRENT. [*Received, November 12th*, 1915].

III.—*The Study of Binary Mixtures. Part I. The Densities and Viscosities of Mixtures containing Phenol.*

By ARTHUR BRAMLEY.

THE study of the physical properties of binary mixtures has engaged the attention for a great many years of a large number of chemists and physicists. It rarely happens that any physical property of a mixture of two substances is exactly the same as that calculated according to a simple mixture rule, but often the difference between the actual and calculated values is small compared with the magni-

ture of the property itself. These differences are generally ascribed to constitutional changes brought about by the interaction of the component substances. When the substances brought together react chemically, the physical properties of the product frequently differ enormously from those of the original substances; on the other hand, when mixing is not accompanied by chemical action, the physical properties of the mixture generally approach closely the values calculated. In a large number of cases where two liquids mix it is very difficult to ascertain whether the mixing is accompanied by chemical action, and still more difficult, if not impossible, to determine the extent of such action. The study of this last class of mixtures really consists in a critical examination of their physical properties, and comparing the values obtained by direct measurement with those calculated according to some formula. It has long been known that the viscosities of mixtures differ from those calculated to a much greater extent than most other physical properties; in contradistinction from other physical properties, the constitutional effect is large compared with the additive value. For this reason, the study of the viscosity of pure and mixed liquids has attracted a considerable amount of attention, but so far no satisfactory explanation of the effect of the interaction of two liquids on the viscosity is forthcoming.

The viscosity-concentration curves of liquid mixtures have been classified by Dunstan and Thole into three divisions according as they deviate but slightly from a straight line, exhibit a maximum, or a minimum. The first class includes mixtures of liquids that are chemically indifferent towards each other, the molecules of which are not associated. In the second class the constituents of each mixture are supposed to react chemically, forming a compound which is the cause of the high viscosity. The third class consists of mixtures of liquids which do not form a compound with one another, and at least one of which contains associated molecules, the low viscosity of the mixture being attributed to the dissociation of complex into simpler molecules as a result of the interaction of the two substances.

This method of classification frequently leaves one in doubt about the category to which some mixtures belong. No mixture has an exactly linear viscosity-composition curve, and it is obviously only necessary to choose two substances which are chemically indifferent towards each other and of about the same viscosity to obtain a mixture having a minimum on its viscosity-composition curve, yet the deviation from linearity may be very small. Further, there are a considerable number of mixtures which show no minimum on their viscosity-composition curves, but the latter lie far below the straight

lines representing the simple mixture rule. Examples of such are mixtures of phenol with benzene, chlorobenzene, nitrobenzene, and acetone, which are described later. The cause of the very great deviations in these cases is undoubtedly the dissociating effect of the second substance on the molecular complexes of phenol. Again, there are many mixtures which have viscosities considerably higher than those calculated according to the simple mixture formula, but their viscosity-composition curves show no maximum. These cases are not provided for in the above system of classification.

Much importance is attached to the existence of a maximum on the viscosity-composition curve by Dunstan and his collaborators (T., 1904, **85**, 817; 1905, **87**, 11; 1907, **91**, 83; 1908, **93**, 1919; 1909, **95**, 1556); Tsakalotos (*Bull. Soc. chim.*, 1908, [iv], **3**, 234), and Faust (*Zeitsch. physikal. Chem.*, 1912, **79**, 97). As regards the cause of a maximum, the general consensus of opinion seems to be that it is the result of the formation of a compound, the latter having a higher viscosity than either of the pure substances. Nearly all attempts to determine the composition of the complex, however, from the position of the maximum have proved futile. This is only to be expected, since in almost every case the position of the maximum point depends on the temperature. Faust (*loc. cit.*) found that with rise in temperature the maximum point on the viscosity-composition curve for mixtures of acetone and chloroform disappears, as also does the minimum point on the acetone–carbon disulphide curve. The mixtures of alkylthiocarbimides and secondary bases examined by Kurnakov and Shemtschushni (*Zeitsch. physikal. Chem.*, 1913, **83**, 481) are exceptional. The viscosity isotherms for these mixtures rise to a definite cusp at a concentration corresponding with equimolecular proportions; moreover, the composition of the mixture which has the maximum viscosity does not vary with temperature. Other investigators, notably Findlay (*Zeitsch. physikal. Chem.*, 1909, **69**, 203) and Denison (*Trans. Faraday Soc.*, 1912, **8**, 20), attribute more importance to the position of maximum deviation of the viscosity curve from a straight line. Denison examined the viscosity curves of a number of mixtures, and found that for each mixture the position of maximum deviation was constant at different temperatures, and occurred at a point corresponding with some simple molecular proportion; this he took to indicate the composition of the compound formed In a large number of cases Denison's test of maximum deviation fails, because not only does it draw no distinction between deviations which are positive and negative, that is, above and below the straight line, but, as will be shown subsequently, the position of maximum deviation frequently varies considerably with the tem-

perature. Findlay (*loc. cit.*), presumably with the object of obtaining conditions approximating to those of corresponding states, measured the viscosities of a number of mixtures at temperatures just below their boiling points. His results failed to reveal any simple relationship between either the maximum viscosity or the maximum deviation and the nature of the compound formed.

Denison's method of analysing the viscosity-composition curves, although yielding definite results in but few cases, suggests another system of classification, which appears simpler and preferable to that of Dunstan and Thole. Two classes only are required:

Class A.—The viscosity-composition curves lie below the straight line joining the viscosities of the pure components.

Class B.—The viscosity-composition curves lie above the straight line joining the viscosities of the pure components.

In general, class A consists of mixtures of substances which do not react chemically with one another to form a compound, the only effect of the interaction of the two pure substances being one of dissociation of complex into simpler molecules. Since there are no linear viscosity isotherms for mixtures, this would imply that all liquids contain some more or less associated molecules, a conclusion for which there is at present no entirely satisfactory criterion. Class B consists of mixtures of substances which react chemically, forming compounds with each other. Some exceptions arise, as, for example, mixtures of phenol and acetone; this pair of substances yields viscosity isotherms of the type A, although the formation of a compound undoubtedly takes place. There are also a number of mixtures giving inflected viscosity isotherms. A discussion of these exceptions will be given subsequently.

The work described below was undertaken with the object of determining what factors influence the viscosity of liquid mixtures, and whether it is possible to ascertain from viscosity measurements the composition of a compound that might exist in a liquid mixture of two substances. For this purpose it was decided to determine the densities and viscosities of mixtures of phenol and several bases of different strengths over as wide a range of temperature as possible. In order to be able to compare the viscosity-composition curves of these mixtures with the general type of curve given by mixtures of phenol and indifferent substances, mixtures of phenol with benzene, chlorobenzene, and nitrobenzene were examined.

Experimental.

In the determination of the densities of the liquids examined, pyknometers of the Sprengel type were employed. For temperatures up to 20° a pyknometer of about 8 c.c. capacity with a bulb

on one limb was used. Two plain Sprengel tubes of about 10 c.c. capacity were employed for the higher temperatures. Duplicate experiments with different pyknometers showed that the figure in the fourth decimal place was trustworthy, but a general consideration of the different factors influencing the determinations of density indicate that this was about the limit of accuracy attained. All the densities are referred to that of water at 4°.

The viscosities were measured by means of viscometers of the Ostwald type. On account of the great differences in the viscosities of the liquids examined, three pairs of viscometers were used. One pair was suitable for liquids of low viscosity, another pair for liquids of intermediate viscosity, and a third pair for liquids of high viscosity. In this way the periods of flow for the different liquids were of about the same order. The hygroscopic nature of the substances used rendered it necessary to protect them from the moisture in the air; this was done by attaching tubes containing anhydrous calcium chloride to the viscometers. The periods of flow were measured by means of two tested stop-watches, which marked off time in fifths of a second. In the calculation of absolute viscosities, Thorpe and Rodgers's value for water at 25°, namely, 0·00891, was taken as standard.

It is well known that in the determination of viscosities of liquids generally, the maintenance at a steady temperature of the bath in which the viscometer is placed is of great importance. Few experiments, however, had been made in the early part of this investigation before it became apparent that, on account of the enormous temperature-coefficients of the viscosity of some of the liquids at the lower temperatures, the precision with which the temperatures of the baths must be maintained was of a high order. This will be evident from the following example: The viscosity of phenol at 20° is 0·1104; at 10° it is 0·2010; for a temperature interval of 10° the viscosity has almost doubled; hence, if an accuracy of 0·1 per cent. is to be attained, the temperature must not vary more than 0·01°. The thermo-regulation of a bath so that its extreme variations never exceed this amount is a matter of some delicacy, especially so when the temperature required is below that of the room. For a constant temperature bath at 0° a 4-litre beaker was filled with a mixture of clean ice broken into small pieces and distilled water. The following arrangement was found to be suitable for temperatures between about 5° and that of the room. The bath consisted of a rectangular copper vessel with two opposite sides of glass, and had a capacity of about 30 litres. Cooling was accomplished in the following way: A coil of about 10 metres of lead tubing (1·2 cm. in diameter) was embedded in

roughly broken ice in a tank of about 30 litres capacity; one end of this coil was connected to a water-tap, and the other to one end of a second coil of similar tubing having a dozen turns of 7·5 cm. diameter. The other end of this coil, which was immersed in the constant-temperature bath, was connected to a pipe leading to a sink. A steady stream of water was run from the tap through the first coil, where it was cooled to a temperature near zero; it then passed through the second coil, thus cooling the water in the bath; finally, it escaped to the sink. The speed of the water was adjusted so that it would cool the bath to a temperature two or three degrees below that required, the final adjustment of the temperature being made by means of an electrical heater actuated by an electrical thermo-regulator of the form described by Gouy (*J. Physique*, 1897, **6**, 479). A full description, with diagrams, of this excellent regulator is given by Barnes (*Phil. Trans.*, 1902, [*A*], **199**, 208). For temperatures between that of the room and 50° the same method was used, excepting, of course, the cooling arrangement, which was dispensed with. Auxiliary heating by means of a small gas flame was necessary for temperatures above 30°. The water in the tank was kept thoroughly mixed by means of a turbine stirrer. Trial runs, extending over a full day, showed that, by the above method, the temperature of the bath could be kept constant within two or three thousandths of a degree. For the more viscous liquids, the temperature-coefficient of viscosity diminishes rapidly with rise in temperature; consequently the very high degree of precision in the maintenance of a constant temperature which is required for the lower temperatures is not so necessary for higher temperatures. The baths used for temperatures above 50° were beakers of 4-litres capacity, and ordinary toluene thermo-regulators were employed. Above 100° the water in the baths was replaced by glycerol, and aniline was used instead of toluene in the regulators.

The substances used were purified as follows:

Phenol.—Pure phenol was distilled, and the middle fraction, which had a constant boiling point, was used.

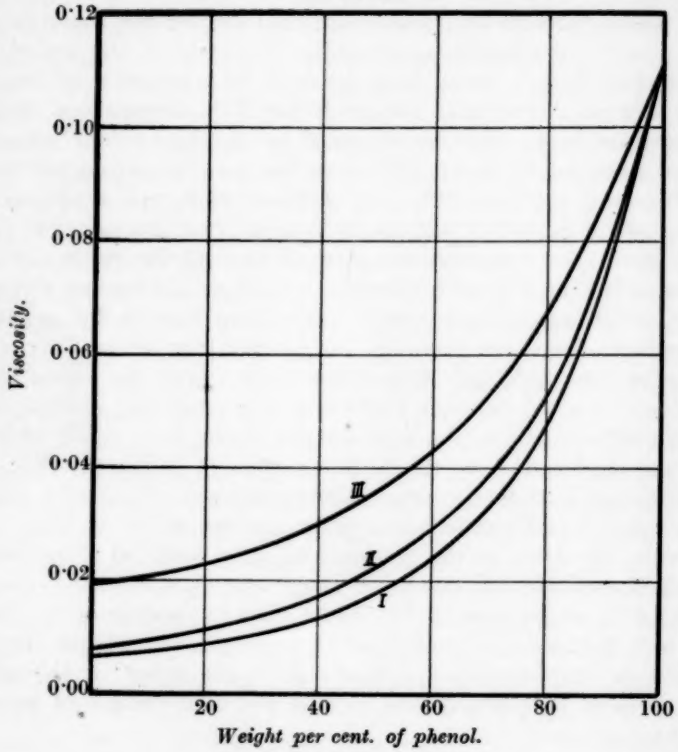
Benzene.—Pure commercial benzene was shaken with successive portions of concentrated sulphuric acid until the latter was no longer coloured; the benzene was then washed several times with water, and dried, first with calcium chloride and afterwards with sodium. Finally, it was distilled through a fractionating column, the portion of constant boiling point being used.

Chlorobenzene.—Kahlbaum's chlorobenzene was kept over anhydrous calcium chloride for a few days, and then distilled. Its boiling point was constant.

Nitrobenzene.—Some nitrobenzene of unknown origin was washed with sodium carbonate solution, then with water, dried over calcium chloride, and distilled. It had a constant boiling point.

Aniline.—Commercial aniline was fractionated several times; finally a quantity was obtained which had a constant boiling point.

FIG. 1.



I. *Phenol and benzene.*
II. ,, ,, *chlorobenzene.*
III. ,, ,, *nitrobenzene.*

Dimethylaniline.—Kahlbaum's preparation was redistilled, and the middle fraction of constant boiling point used.

p-*Toluidine, Diphenylamine, and Diphenylmethylamine.*—These substances, obtained from Kahlbaum, were redistilled under diminished pressure, the first and last portions being rejected.

Quinoline.—Kahlbaum's synthetic quinoline was allowed to remain in contact with solid potassium hydroxide for several days, and then distilled; a portion of constant boiling point was obtained.

Pyridine.—Pure commercial pyridine was kept in contact with

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solid potassium hydroxide for several days, and then fractionated by distillation. This process was repeated several times, and ultimately a quantity was obtained which had a range of boiling point less than one-tenth of a degree.

Phenetole.—This substance, obtained from Kahlbaum, was redistilled. It had a constant boiling point.

Acetone.—Commercially pure acetone was treated with aqueous potassium permanganate solution, and allowed to remain for three or four days, more permanganate solution being added as the colour disappeared. The acetone was distilled off on the steam-bath, dried over calcium chloride, and finally distilled, using a fractionating column. From 2500 c.c. of commercial acetone, 1500 c.c. were obtained, which had a range of boiling point of less than one-tenth of a degree.

Mixtures of phenol with (*a*) benzene, (*b*) chlorobenzene, and (*c*) nitrobenzene were examined at one temperature only, namely, 20°. The values obtained are given in tables I*a*, I*b*, and I*c*, and Fig. 1 represents graphically the relations between the viscosity and composition of these mixtures. The density-composition curves for these mixtures are almost straight lines; they lie very slightly below the linear.

TABLE I*a*.

Mixtures of Phenol and Benzene.

Weight per cent. of phenol.	Density at 20°.	Viscosity at 20°.
0·00	0·8772	0·00629
6·04	0·8880	0·00683
9·84	0·8949	0·00724
20·01	0·9133	0·00865
32·40	0·9370	0·01126
42·09	0·9549	0·01401
53·02	0·9766	0·01911
63·65	0·9976	0·02642
74·11	1·0194	0·03811
83·20	1·0383	0·0535
100·00	1·0752	0·1104

TABLE I*b*.

Mixtures of Phenol and Chlorobenzene.

Weigh per cent. of phenol.	Density at 20°.	Viscosity at 20°.
0·00	1·1051	0·00768
4·93	1·1034	0·00825
9·78	1·1018	0·00888
21·73	1·0980	0·01122
30·43	1·0954	0·01374
38·90	1·0930	0·01673
49·90	1·0898	0·02218
58·15	1·0874	0·02748
71·41	1·0836	0·04070
81·45	1·0806	0·05555
100·00	1·0752	0·1104

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TABLE Ic.

Mixtures of Phenol and Nitrobenzene.

Weight per cent. of phenol.	Density at 20°.	Viscosity at 20°.
0·00	1·2021	0·01931
4·16	1·1957	0·01975
8·84	1·1888	0·02041
18·12	1·1756	0·02208
27·41	1·1635	0·02460
37·96	1·1495	0·02845
49·73	1·1346	0·0353
58·64	1·1233	0·0419
71·03	1·1085	0·0540
84·68	1·0927	0·0759
100·00	1·0752	0·1104

The densities and viscosities of mixtures of phenol and aniline were determined for a number of temperatures ranging from 20° to 125°. Tables II and II*a* contain the results obtained, and the viscosity isotherms are shown in Fig. 2. The viscosity-composition curves were drawn on a large scale for each temperature, and the position of maximum deviation from the straight line joining the viscosities of the two components was determined. The composition of the mixtures which show the greatest divergence in viscosity from the values calculated according to the simple mixture rule, together with the corresponding temperatures, are given in table II*b*. These quantities are represented graphically in the small curve inset in Fig. 2. The density curves for these mixtures are almost straight lines, the densities found being slightly higher than those calculated. The viscosities of mixtures of phenol and aniline have been measured for one temperature, namely, 35°, by Thole, Dunstan, and Mussell (T., 1913, **103**, 1114).

FIG. 2.

Phenol and aniline.

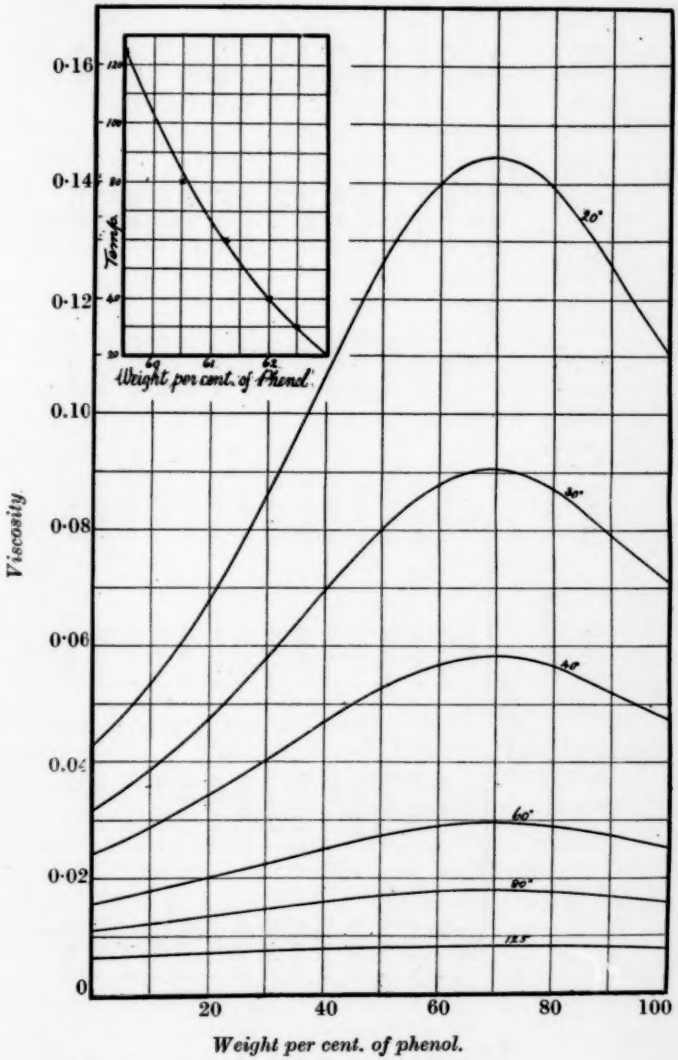


Table II.

Mixtures of Phenol and Aniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	30°	40°	60°	80°	30°	40°	60°	80°
0·00	1·0131	1·0045	0·9872	0·9700	0·03145	0·02405	0·0154	0·01100
7·58	1·0185	1·0099	0·9925	0·9752	0·0366	0·0274	0·0169	0·01175
15·96	1·0242	1·0156	0·9982	0·9809	0·0434	0·0315	0·0188	0·01280
23·33	1·0292	1·0206	1·0032	0·9858	0·0507	0·0361	0·02083	0·01375
31·65	1·0347	1·0260	1·0086	0·9911	0·0595	0·0410	0·02285	0·01480
39·14	1·0394	1·0307	1·0133	0·9959	0·0685	0·0461	0·02485	0·01570
47·17	1·0442	1·0355	1·0180	1·0005	0·0770	0·0510	0·0267	0·01662
54·00	1·0448	1·0394	1·0220	1·0047	0·0836	0·0545	0·0279	0·01720
61·84	1·0521	1·0434	1·0259	1·0085	0·0889	0·0573	0·0290	0·01768
69·28	1·0557	1·0470	1·0296	1·0122	0·0907	0·0583	0·0294	0·01793
76·86	1·0590	1·0504	1·0330	1·0156	0·0889	0·0573	0·0292	0·01777
84·80	1·0617	1·0531	1·0358	1·0185	0·0834	0·0546	0·02835	0·01745
92·50	1·0646	1·0561	1·0388	1·0215	0·0768	0·0511	0·0269	0·01670
100·00	1·0668	1·0584	1·0414	1·0242	0·0709	0·0476	0·0252	0·01580

TABLE II*a*.

Mixtures of Phenol and Aniline.

Weight per cent. of phenol.	Densities.		Viscosities.	
	20°.	125°.	20°.	125°.
0·00	1·0219	0·9288	0·0428	0·00637
7·94	1·0276	0·9342	0·0509	0·00666
15·31	1·0326	0·9390	0·0610	0·00693
23·34	1·0380	0·9436	0·0735	0·00723
31·28	1·0434	0·9482	0·0889	0·00749
39·39	1·0485	0·9527	0·1059	0·00770
47·56	1·0532	0·9571	0·1215	0·00788
53·81	1·0569	0·9606	0·1320	0·00799
62·50	1·0611	0·9648	0·1418	0·00811
69·52	1·0644	0·9690	0·1447	0·00817
77·02	1·0675	0·9727	0·1421	0·00818
85·02	1·0704	0·9762	0·1331	0·00813
92·28	1·0729	0·9795	0·1221	0·00797
100·00	1·0750	0·9828	0·1104	0·00770

TABLE II*b*.

Mixtures of Phenol and Aniline.

Weight per cent. of phenol ...	63·0	62·5	62·0	61·25	60·5	59·5
Temperature.....	20°	30°	40°	60°	80°	125°

Mixtures of phenetole and aniline were examined at several temperatures ranging from 0° to 80°. The figures obtained for the densities and viscosities are given in table III. The density-composition curves for mixtures of these substances are straight lines, the values found coinciding with those calculated. Fig. 3 contains the viscosity isotherms, the character of which, it will be seen, is altogether different from that of the corresponding curves for mixtures of phenol and aniline.

FIG. 3.

Aniline and phenetole.

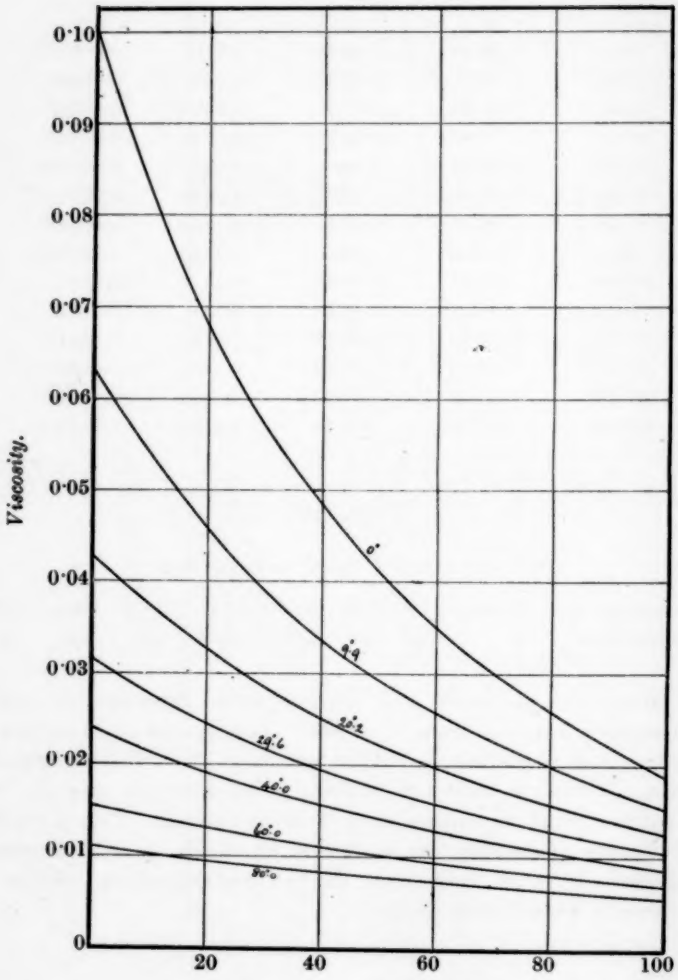


Table III

Mixtures of Phenetole and Aniline.

Weight per cent. of phenetole.	Densities.							Viscosities.						
	0°	9·9°	20·2°	29·6°	40·0°	60·0°	80·0°	0°	9·9°	20·2°.	29·6°	40·0°	60·0°	80·0°
0·00	1·0390	1·0303	1·0214	1·0134	1·0045	0·9872	0·9700	0·1005	0·0631	0·0426	0·0315	0·02405	0·01545	0·01100
11·74	1·0326	1·0239	1·0149	1·0070	0·9980	0·9809	0·9637	0·0799	0·0523	0·0364	0·0270	0·02080	0·01395	0·01013
21·75	1·0272	1·0184	1·0094	1·0014	0·9922	0·9748	0·9573	0·0655	0·0443	0·0317	0·0238	0·01865	0·01280	0·00944
32·30	1·0216	1·0128	1·0037	0·9956	0·9864	0·9688	0·9511	0·0548	0·0375	0·0275	0·02115	0·01675	0·01171	0·00877
43·68	1·0155	1·0066	0·9974	0·9893	0·9801	0·9623	0·9444	0·0451	0·0321	0·0239	0·01870	0·01500	0·01065	0·00814
54·66	1·0096	1·0007	0·9916	0·9833	0·9740	0·9560	0·9379	0·0379	0·0276	0·0210	0·01670	0·01355	0·00977	0·00758
65·69	1·0036	0·9946	0·9854	0·9771	0·9677	0·9497	0·9315	0·03205	0·02385	0·0184	0·01495	0·01225	0·00896	0·00706
76·54	0·9978	0·9888	0·9795	0·9712	0·9616	0·9434	0·9249	0·02720	0·02075	0·01630	0·01335	0·01106	0·00826	0·00659
88·49	0·9914	0·9823	0·9729	0·9644	0·9547	0·9363	0·9176	0·02265	0·01780	0·01428	0·01169	0·00982	0·00753	0·00603
100·0	0·9852	0·9760	0·9666	0·9580	0·9483	0·9298	0·9110	0·01860	0·01530	0·01240	0·01030	0·00875	0·00687	0·00558

Tables IV and IV*a* contain the densities and viscosities of mixtures of phenol and *p*-toluidine for several temperatures between 40° and 175°. The densities are somewhat higher than the calculated values; consequently, the density curve is slightly concave towards the composition axis. The viscosity curves are shown in Fig. 4. Table IV*b* contains the composition of mixtures the viscosities of which show a maximum deviation from the calculated values, together with the corresponding temperatures. These were obtained as already described for phenol and aniline, and the small curve inset in Fig. 4 depicts the relationship between the two.

This mixture has been examined at 30° by Thole, Dunstan, and Mussell (*loc. cit.*), who found that the maximum point on the viscosity-composition curve was at 63 per cent. of phenol. According to the experiments described in this paper, the position of the maximum point on the viscosity curve corresponds with a composition of 67 per cent. of phenol, and since, in this case, the position of the maximum does not vary appreciably with the temperature, there appears to be a discrepancy of about 4 per cent. in the composition of the mixture of maximum viscosity. Independent experiments carried out in this laboratory, in which Kahlbaum's chemicals, redistilled before use, were employed, gave the following results for a temperature of 31·5°:

Weight per cent. of phenol	50·6	63·3	66·0	68·8	70·7	79·1	86·0
Viscosity	0·0846	0·0921	0·0931	0·0931	0·0926	0·0867	0·0803

These figures indicate a maximum viscosity at a point corresponding with a composition of about 67·5 per cent. of phenol, which agrees well with the value found by the author.

FIG. 4.

Phenol and p-*toluidine.*

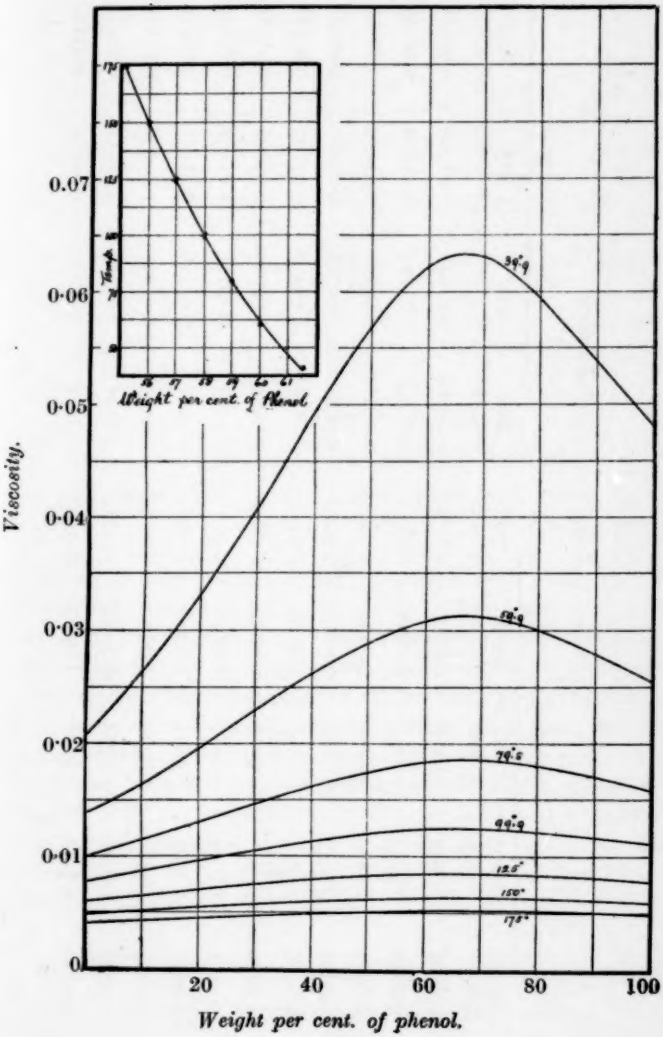


TABLE IV.

Mixtures of Phenol and p-*Toluidine.*

Weight per cent. of phenol.	Densities.					Viscosities.				
	39·9°	59·9°	79·8°	99·9°	125°	39·9°	59·9°	79·8°	99·9°	125°
0·00	0·9703	0·9534	0·9365	0·9189	0·8962	0·02080	0·01398	0·01006	0·00776	0·00608
9·85	0·9808	0·9640	0·9470	0·9295	0·9068	0·02632	0·01649	0·01149	0·00869	0·00655
20·67	0·9913	0·9744	0·9574	0·9398	0·9172	0·03352	0·01983	0·01323	0·00969	0·00706
29·86	1·0004	0·9835	0·9665	0·9488	0·9261	0·04090	0·02283	0·01469	0·01050	0·00749
38·57	1·0087	0·9919	0·9750	0·9575	0·9348	0·0482	0·02564	0·01600	0·01123	0·00790
46·25	1·0160	0·9991	0·9820	0·9645	0·9418	0·0543	0·02810	0·01705	0·01175	0·00820
55·09	1·0239	1·0069	0·9898	0·9723	0·9495	0·06015	0·03015	0·01805	0·01226	0·00842
62·70	1·0305	1·0135	0·9965	0·9795	0·9567	0·0629	0·03115	0·01858	0·01245	0·00851
71·11	1·0372	1·0201	1·0031	0·9856	0·9628	0·0627	0·03110	0·01857	0·01240	0·00847
80·19	1·0441	1·0270	1·0099	0·9924	0·9696	0·05915	0·02990	0·01804	0·01210	0·00830
89·76	1·0512	1·0340	1·0170	0·9995	0·9766	0·0538	0·02780	0·01711	0·01171	0·00806
100·00	1·0585	1·0414	1·0243	1·0065	0·9833	0·0479	0·02520	0·01581	0·01115	0·00770

TABLE IV*a*.

Mixtures of Phenol and p-*Toluidine.*

Weight per cent. of phenol.	Densities.		Viscosities.	
	150°.	175°.	150°.	175°.
0·00	0·8734	0·8502	0·00491	0·00423
16·62	0·8898	0·8668	0·00541	0·00456
23·11	0·8961	0·8732	0·00560	0·00468
34·42	0·9069	0·8842	0·00594	0·00490
38·24	0·9105	0·8878	0·00603	0·00496
45·61	0·9172	0·8943	0·00619	0·00507
56·31	0·9264	0·9034	0·00636	0·00517
65·69	0·9341	0·9110	0·00641	0·00520
76·25	0·9421	0·9188	0·00635	0·00515
79·43	0·9443	0·9210	0·00630	0·00512
86·34	0·9491	0·9256	0·00618	0·00508
100·00	0·9572	0·9337	0·00592	0·00492

TABLE IV*b*.

Mixtures of Phenol and p-*Toluidine.*

Weight per cent. of phenol..	61·5	60·0	59·0	58·0	57·0	56·0	55·0
Temperature	39·9°	59·9°	79·8°	99·9°	125°	150°	175°

Mixtures of phenol and dimethylaniline were examined at eight temperatures between 10° and 180°. The figures obtained are given in tables V and V*a*. The viscosity-composition curves are given in Fig. 5. On account of the sinuous nature of these curves, the deviations from the straight line are both positive and negative, that is, some of the viscosities are greater and some less than the values calculated according to the simple mixture rule. Table V*b* contains the composition of mixtures the viscosities of which show a maximum positive deviation and the corresponding temperatures. The connexion between the two is shown graphically by the curve inset in Fig. 5. The densities of these mixtures are but slightly higher than the calculated values.

TABLE V*b*.

Mixtures of Phenol and Dimethylaniline.

Weight per cent. of phenol.....	87·5	84·0	82·0	80·0	78·0	76·0	73·0	71·5
Temperature	10°	20°	29·8°	40·2°	59·9°	80·0°	126·0°	177°

FIG. 5.

Phenol and dimethylaniline.

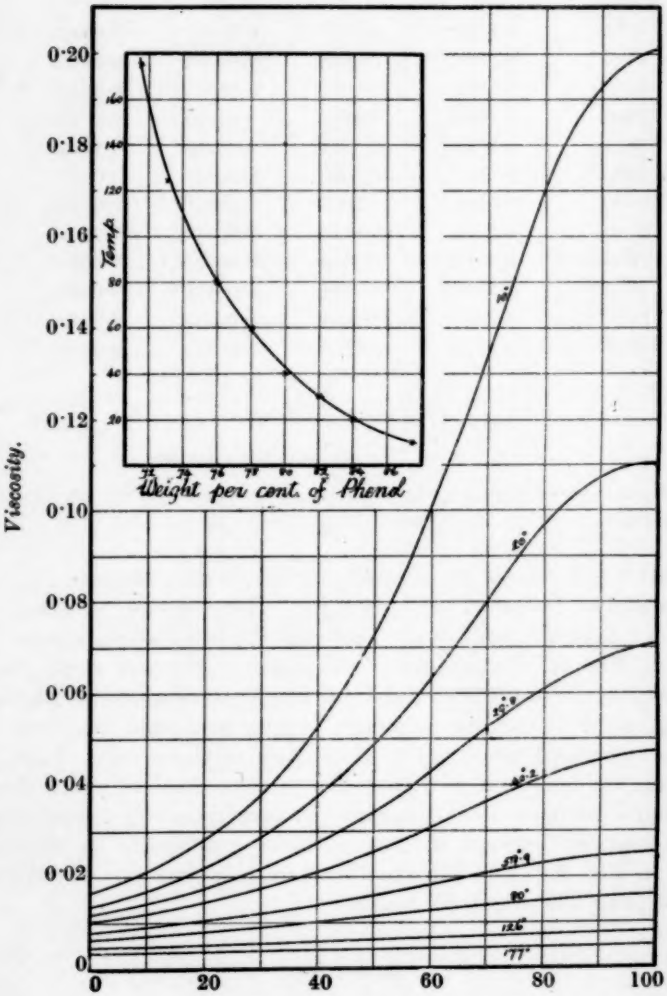


Table V.

Mixtures of Phenol and Dimethylaniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	10°	20°	126°	177°	10°	20°	126°	177°
0·00	0·9647	0·9564	0·8679	0·8225	0·01654	0·01387	0·00461	0·00341
9·07	0·9752	0·9670	0·8776	0·8318	0·02076	0·01684	0·00482	0·00352
17·30	0·9851	0·9768	0·8863	0·8403	0·02586	0·02045	0·00508	0·00362
23·94	0·9932	0·9849	0·8939	0·8472	0·03145	0·02415	0·00531	0·00372
33·08	1·0041	0·9959	0·9040	0·8568	0·04185	0·03085	0·00565	0·00386
40·39	1·0136	1·0053	0·9127	0·8647	0·05315	0·0377	0·00594	0·00398
48·27	1·0236	1·0150	0·9216	0·8733	0·0696	0·0470	0·00627	0·00410
55·75	1·0327	1·0243	0·9302	0·8817	0·0869	0·0564	0·00653	0·00422
62·82	1·0413	1·0330	0·9387	0·8895	0·1094	0·0675	0·00680	0·00432
69·97	1·0500	1·0416	0·9471	0·8978	0·1347	0·0801	0·00703	0·00442
78·14	1·0595	1·0512	0·9564	0·9069	0·1639	0·0940	0·00728	0·00453
85·39	1·0678	1·0595	0·9648	0·9152	0·1850	0·1040	0·00745	0·00460
92·76	1·0759	1·0676	0·9734	0·9237	0·1964	0·1087	0·00761	0·00467
100·00	1·0835	1·0752	0·9815	0·9315	0·2010	0·1104	0·00770	0·00490

Table Va.

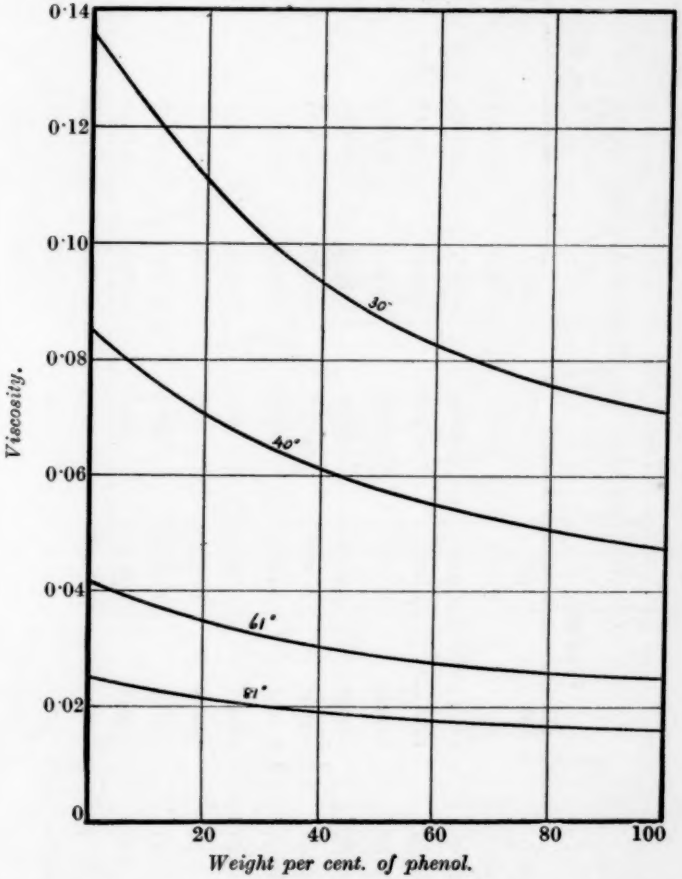
Mixtures of Phenol and Dimethylaniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	29·8°	40·2°	59·9°	80·0°	29·8°	40·2°	59·9°	80·0°
0·00	0·9482	0·9400	0·9234	0·9070	0·01173	0·01021	0·00799	0·00658
7·93	0·9574	0·9492	0·9325	0·9159	0·01351	0·01159	0·00878	0·00707
16·61	0·9677	0·9593	0·9425	0·9258	0·01629	0·01354	0·01001	0·00782
24·60	0·9772	0·9688	0·9520	0·9352	0·01936	0·01570	0·01123	0·00852
32·71	0·9872	0·9788	0·9619	0·9449	0·02315	0·01840	0·01267	0·00937
41·46	0·9981	0·9895	0·9724	0·9553	0·0283	0·02185	0·01428	0·01025
49·19	1·0076	0·9990	0·9818	0·9645	0·0333	0·02510	0·01587	0·01119
56·14	1·0158	1·0073	0·9899	0·9726	0·0393	0·02855	0·01760	0·01213
63·95	1·0252	1·0166	0·9991	0·9817	0·04705	0·0334	0·01960	0·01312
70·99	1·0329	1·0243	1·0069	0·9895	0·05325	0·03715	0·02100	0·01379
78·83	1·0431	1·0346	1·0171	0·9997	0·06025	0·0415	0·02270	0·01472
86·08	1·0516	1·0431	1·0256	1·0082	0·0648	0·0440	0·02380	0·01523
93·19	1·0594	1·0509	1·0335	1·0162	0·0686	0·0459	0·02665	0·01567
100·00	1·0668	1·0584	1·0414	1·0242	0·0709	0·0474	0·02530	0·01585

Phenol and diphenylamine mixtures were examined at four temperatures between 30° and 81°, and the results obtained are given in table VI. The figures in brackets for the viscosities of diphenylamine at 30° and 40° were obtained by extrapolation. Fig. 6 shows graphically the relationship between the viscosity and composition of these mixtures. The density curves in this case

FIG. 6.

Phenyl and diphenylamine.



are straight lines. A few mixtures of these two compounds have been examined at 50° by Thole, Dunstan, and Mussell (*loc. cit.*).

Mixtures of phenol and diphenylmethylamine were examined at six temperatures between 10° and 80°, and the measurements are recorded in tables VII and VII*a*. The density curves are almost straight lines, the calculated densities being slightly higher than

Table VI.

Mixtures of Phenol and Diphenylamine.

Weight per cent. of phenol.	Densities.				Viscosities.			
	30°	40°	61°	81°	30°	40°	61°	81°
0·0	—	—	1·0543	1·0377	(0·1357)	(0·0852)	0·0417	0·02525
7·87	1·0790	1·0711	1·0533	1·0366	0·1257	0·0795	0·0383	0·0236
15·18	1·0780	1·0700	1·0523	1·0356	0·1165	0·0743	0·0359	0·0224
23·29	1·0769	1·0689	1·0511	1·0344	0·1072	0·0693	0·0339	0·02125
30·87	1·0759	1·0678	1·0501	1·0333	0·1003	0·0652	0·03225	0·02025
38·60	1·0749	1·0668	1·0490	1·0321	0·0947	0·0620	0·03085	0·01955
46·56	1·0738	1·0656	1·0478	1·0309	0·0898	0·0591	0·0296	0·01880
53·43	1·0729	1·0647	1·0470	1·0300	0·0861	0·0568	0·02865	0·01828
59·65	1·0721	1·0639	1·0461	1·0292	0·0828	0·0551	0·0279	0·01782
68·84	1·0709	1·0626	1·0448	1·0278	0·0791	0·0528	0·02685	0·01723
76·60	1·0699	1·0616	1·0438	1·0268	0·0765	0·0513	0·0262	0·01680
84·59	1·0688	1·0605	1·0427	1·0256	0·0742	0·0498	0·02565	0·01640
92·04	1·0678	1·0595	1·0416	1·0245	0·07255	0·04845	0·0253	0·01610
100·00	1·0667	1·0584	1·0405	1·0233	0·0709	0·0474	0·0251	0·01575

the observed values. Fig. 7 shows the connexion between the viscosities and compositions of these mixtures.

FIG. 7.

Phenol and diphenylmethylamine.

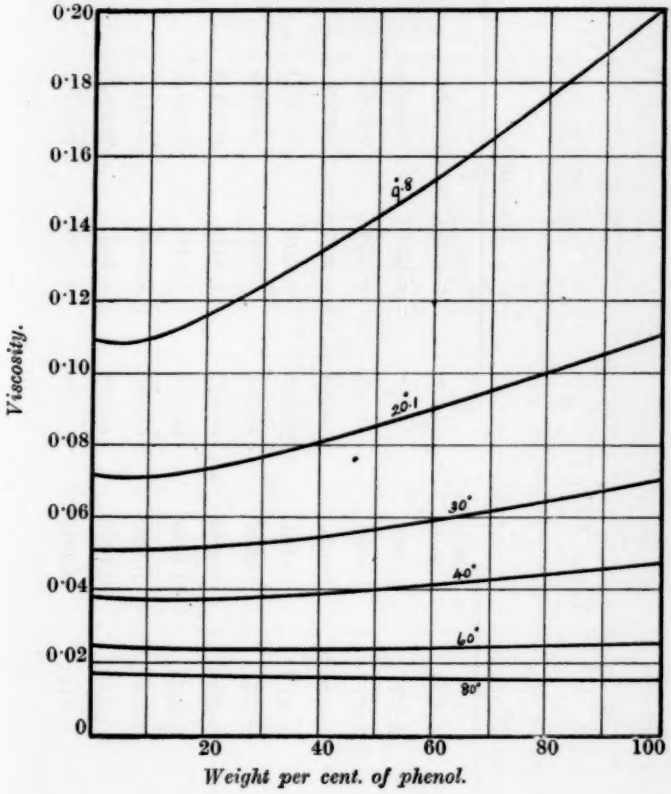


TABLE VII.

Mixtures of Phenol and Diphenylmethylamine.

Weight per cent. of phenol.	Densities.		Viscosities.	
	9·8°	20·1°	9·8°	20·1°
0·00	1·0595	1·0515	0·1096	0·0722
4·92	1·0605	1·0523	0·1090	0·0708
9·48	1·0615	1·0532	0·1097	0·0715
17·18	1·0632	1·0548	0·1145	0·0730
27·69	1·0657	1·0572	0·1226	0·0764
36·92	1·0679	1·0593	0·1306	0·0798
48·42	1·0708	1·0621	0·1411	0·0845
56·87	1·0728	1·0641	0·1502	0·0885
67·10	1·0753	1·0665	0·1614	0·0935
78·79	1·0782	1·0693	0·1752	0·0995
89·30	1·0809	1·0720	0·1877	0·1048
100·00	1·0836	1·0750	0·2010	0·1104

TABLE VII*a*.

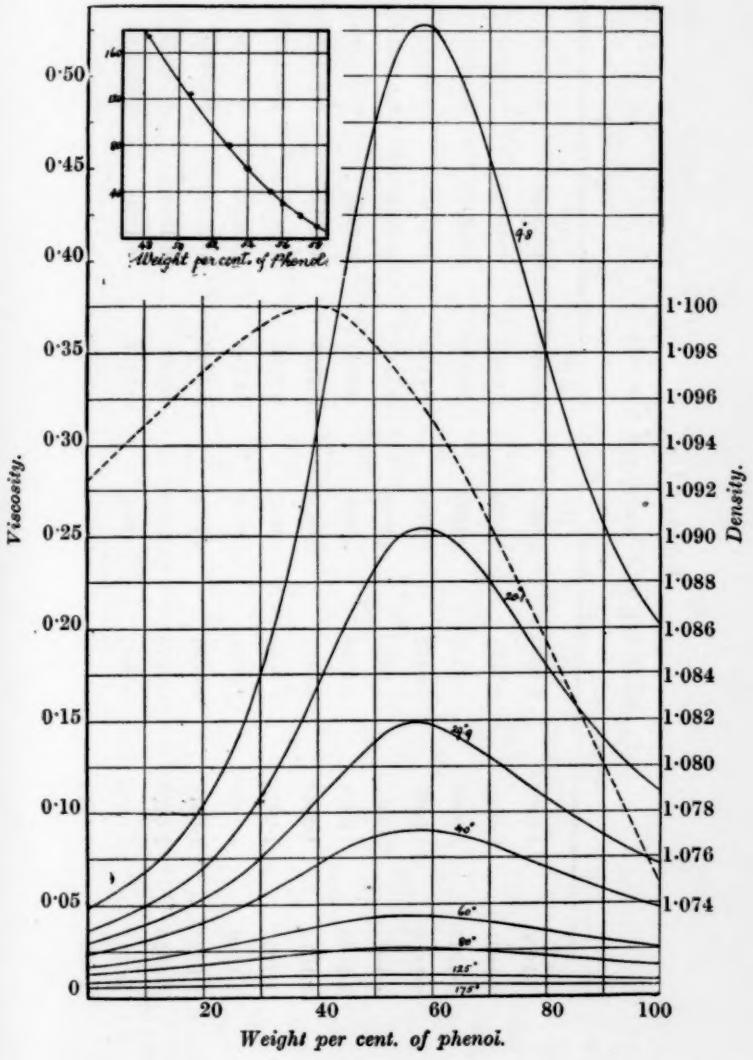
Mixtures of Phenol and Diphenylmethylamine.

Weight per cent. of phenol.	Densities.				Viscosities.			
	30°	40°	60°	80°	30°	40°	60°	80°
0·00	1·0438	1·0359	1·0198	1·0040	0·0513	0·03835	0·02480	0·01735
4·98	1·0449	1·0369	1·0207	1·0048	0·0510	0·03785	0·02435	0·01708
10·21	1·0461	1·0379	1·0217	1·0058	0·0513	0·0376	0·0240	0·01682
20·04	1·0483	1·0401	1·0237	1·0076	0·0519	0·0377	0·0237	0·01650
35·34	1·0519	1·0435	1·0269	1·0104	0·0542	0·0388	0·02375	0·01624
49·87	1·0552	1·0467	1·0301	1·0136	0·0570	0·0402	0·02395	0·01603
62·12	1·0581	1·0495	1·0328	1·0164	0·0597	0·0415	0·02415	0·01594
73·58	1·0607	1·0521	1·0354	1·0188	0·0626	0·0428	0·02445	0·01589
82·22	1·0627	1·0542	1·0373	1·0206	0·0650	0·0440	0·0247	0·01585
90·05	1·0645	1·0560	1·0391	1·0223	0·0673	0·0451	0·02495	0·01586
100·00	1·0668	1·0584	1·0414	1·0242	0·0709	0·0474	0·0253	0·01585

The densities and viscosities of mixtures of phenol and quinoline were determined for eight temperatures ranging from 9·8° to 175°,

FIG. 8.

Phenol and quinoline.



and the measurements are recorded in tables VIII and VIII*a*. Fig. 8 contains the viscosity curves, and the small curve inset shows the connexion between the temperature and composition of the

Table VIII.

Mixtures of Phenol and Quinoline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	9·8°	20·1°	125°	175°	9·8°	20·1°	125°	175°
0·00	1·1004	1·0925	1·0085	0·9673	0·04805	0·03635	0·00786	0·00547
7·54	1·1021	1·0944	1·0103	0·9687	0·0619	0·04595	0·00837	0·00564
14·56	1·1037	1·0960	1·0119	0·9698	0·0810	0·05725	0·00901	0·00588
22·73	1·1056	1·0977	1·0133	0·9707	0·1170	0·0785	0·00988	0·00622
29·76	1·1071	1·0992	1·0140	0·9705	0·1677	0·1058	0·01064	0·00642
37·52	1·1078	1·0999	1·0139	0·9696	0·2644	0·1503	0·01121	0·00650
45·08	1·1074	1·0994	1·0127	0·9678	0·3750	0·2031	0·01155	0·00652
53·20	1·1057	1·0977	1·0099	0·9643	0·5065	0·2452	0·01158	0·00649
60·30	1·1030	1·0950	1·0065	0·9602	0·5259	0·2529	0·01119	0·00632
68·21	1·0994	1·0914	1·0021	0·9550	0·4740	0·2327	0·01055	0·00606
76·88	1·0950	1·0869	0·9969	0·9492	0·3836	0·1941	0·00969	0·00570
83·37	1·0916	1·0835	0·9927	0·9445	0·3156	0·1660	0·00918	0·00542
92·06	1·0875	1·0791	0·9876	0·9389	0·2420	0·1337	0·00837	0·00513
100·00	1·0836	1·0750	0·9828	0·9337	0·2010	0·1104	0·00770	0·00492

TABLE VIII*a*.

Mixtures of Quinoline and Phenol.

Weight per cent. of phenol.	Densities.				Viscosities.			
	29·9°	40°	60°	80°	29·9°	40°	60°	80°
0·00	1·0851	1·0773	1·0615	1·0458	0·02943	0·02384	0·01671	0·01250
7·77	1·0870	1·0792	1·0635	1·0478	0·03645	0·02885	0·01950	0·01424
14·92	1·0886	1·0808	1·0651	1·0494	0·04495	0·03455	0·02245	0·01603
21·96	1·0904	1·0823	1·0666	1·0509	0·05605	0·04195	0·02615	0·01809
29·82	1·0917	1·0838	1·0679	1·0518	0·07425	0·05335	0·03120	0·02071
37·14	1·0924	1·0843	1·0682	1·0521	0·0965	0·0660	0·03645	0·02308
44·62	1·0917	1·0837	1·0675	1·0514	0·1221	0·0795	0·0410	0·02520
52·31	1·0901	1·0820	1·0658	1·0496	0·1436	0·0887	0·0436	0·02610
59·89	1·0874	1·0793	1·0629	1·0465	0·1480	0·0904	0·0440	0·02582
67·92	1·0837	1·0755	1·0590	1·0425	0·1344	0·0839	0·0410	0·02415
75·75	1·0795	1·0713	1·0548	1·0382	0·1177	0·0748	0·0371	0·02232
83·49	1·0756	1·0672	1·0503	1·0335	0·1010	0·0656	0·03315	0·02028
91·79	1·0711	1·0628	1·0458	1·0288	0·0844	0·05525	0·02875	0·01786
100·00	1·0668	1·0584	1·0414	1·0242	0·0709	0·0476	0·0252	0·01580

mixture which has a viscosity deviating to the greatest extent from the calculated value. The data from which this curve is drawn were obtained from the viscosity curves as previously indicated, and these are enumerated in the following table:

TABLE VIII*b*.

Mixtures of Phenol and Quinoline.

Weight per cent. of phenol	58·0	57·0	56·0	55·5	54·0	53·0	50·5	48·0
Temperature	9·8°	20·1°	29·9°	40·0°	60·0°	80·0°	125°	175°

The broken line curve in Fig. 8 is the density curve for 20·1°. Unlike all the other mixtures described in this paper, the density-composition curve for mixtures of phenol and quinoline has a very pronounced maximum. Moreover, this maximum does not become less marked with rise in temperature; the density curves for the other temperatures run very approximately parallel to the one shown in the figure.

Mixtures of phenol and pyridine were examined at seven temperatures ranging from 10° to 110°, and the results are set out in tables IX and IX*a*. In Fig. 9 are given the viscosity curves. The scale of viscosities for the three highest temperatures, 60°, 80°, and 110°, is considerably extended in order to bring out more clearly the character of the curves. Inset in Fig. 9 is the curve connecting temperature with the composition of the mixture which shows a maximum positive deviation in viscosity. Data for the construction of this curve are given in table IX*b*.

TABLE IX*b*.

Mixtures of Phenol and Pyridine.

Weight per cent. of phenol	93·0	88·0	84·5	82·0	77·0	73·5	70·0
Temperature	10°	20°	30°	40°	60°	80°	110°

The densities of mixtures of these two substances show a considerable deviation from the calculated values; this is especially so with those mixtures containing a greater proportion of phenol. The broken line curve shows the connexion between density and composition for one temperature, namely, 20°. The density curves for all the other temperatures run closely parallel to this.

FIG. 9.

Phenol and pyridine.

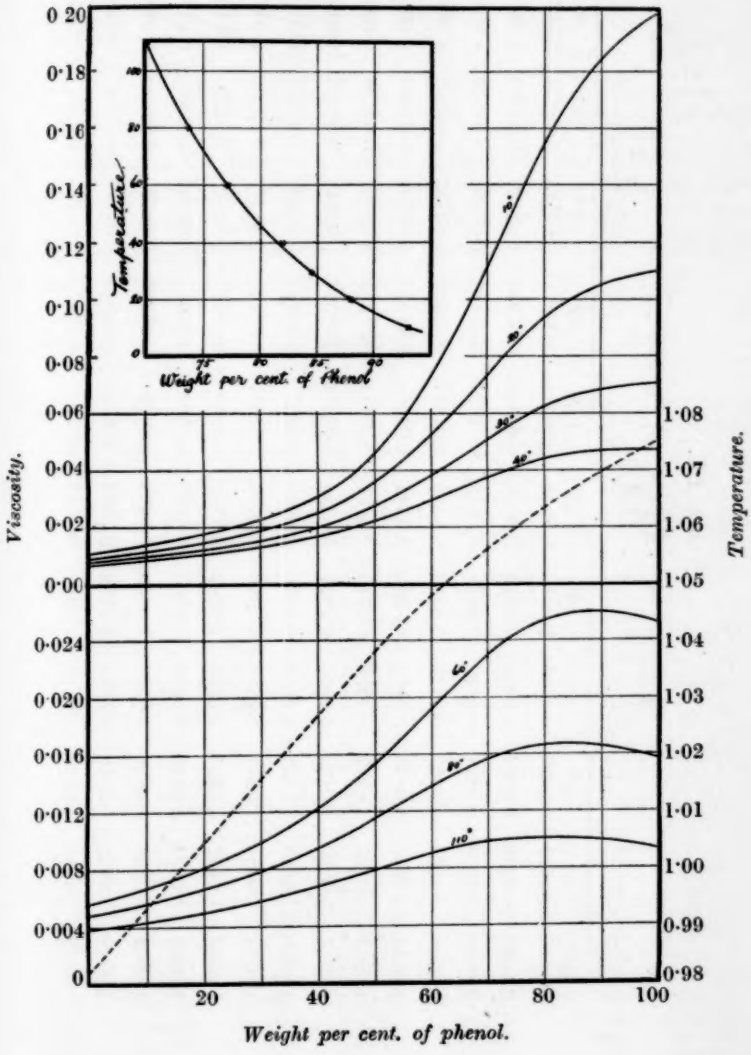


Table IX.

Mixtures of Phenol and Pyridine.

Weight per cent. of phenol	Densities.						Viscosities.					
	20°	30°	40°	60°	80°	110°	20°	30°	40°	60°	80°	110°
0·00	0·9819	0·9723	0·9627	0·9424	0·9218	0·8900	0·00941	0·00821	0·00714	0·00578	0·00487	0·00385
8·30	0·9916	0·9820	0·9724	0·9524	0·9324	0·9014	0·01109	0·00940	0·00828	0·00656	0·00544	0·00428
16·12	1·0005	0·9909	0·9814	0·9620	0·9428	0·9119	0·01321	0·01106	0·00965	0·00753	0·00614	0·00475
24·36	1·0096	1·0002	0·9909	0·9720	0·9532	0·9234	0·01597	0·01339	0·01152	0·00879	0·00713	0·00535
32·58	1·0187	1·0096	1·0005	0·9821	0·9639	0·9347	0·02010	0·01634	0·01389	0·01032	0·00815	0·00606
38·94	1·0258	1·0167	1·0077	0·9897	0·9718	0·9430	0·02411	0·01963	0·01631	0·01198	0·00934	0·00669
47·13	1·0349	1·0260	1·0173	0·9995	0·9821	0·9535	0·03215	0·02515	0·02042	0·01436	0·01077	0·00751
54·96	1·0429	1·0343	1·0257	1·0083	0·9910	0·9626	0·0437	0·03245	0·02560	0·01727	0·01263	0·00841
63·81	1·0514	1·0426	1·0341	1·0168	0·9995	0·9719	0·05945	0·0429	0·03245	0·02065	0·01446	0·00935
70·49	1·0568	1·0482	1·0397	1·0226	1·0053	0·9779	0·0748	0·0517	0·0380	0·0230	0·01580	0·00988
77·94	1·0620	1·0534	1·0449	1·0279	1·0107	0·9833	0·0907	0·0604	0·04305	0·0250	0·01655	0·01013
85·17	1·0668	1·0583	1·0498	1·0327	1·0155	0·9878	0·1004	0·06625	0·0459	0·0259	0·01670	0·01012
92·45	1·0710	1·0625	1·0540	1·0369	1·0198	0·9923	0·1072	0·06915	0·04705	0·0259	0·01650	0·00985
100·00	1·0752	1·0668	1·0584	1·0414	1·0242	0·9967	0·1104	0·0709	0·0474	0·0252	0·01580	0·00941

Table IX*a*.

Mixtures of Phenol and Pyridine.

Weight per cent. of phenol.	Density at 10°	Viscosity at 10°	Weight per cent. of phenol.	Density at 10°	Viscosity at 10°
0·00	0·9916	0·01108	58·46	1·0544	0·0680
17·26	1·0101	0·01594	66·99	1·0618	0·0988
26·01	1·0196	0·02050	76·81	1·0700	0·1416
35·14	1·0294	0·02675	82·86	1·0742	0·1644
45·48	1·0412	0·0376	91·89	1·0787	0·1880
51·89	1·0479	0·0505	100·00	1·0836	0·2010

Tables X and X*a* contain a record of densities and viscosities of mixtures of phenol and acetone for five temperatures ranging from 9·95° to 49·8°. The viscosity curves are given in Fig. 10. The densities of these mixtures are almost the same as those calculated; the density curves are almost straight lines.

Table X.

Mixtures of Phenol and Acetone.

Weight per cent. of phenol.	Densities.		Viscosities.	
	9·95°	20·05°	9·95°	20·05°
0·00	0·8031	0·7912	0·00360	0·00323
14·19	0·8425	0·8315	0·00486	0·00429
26·72	0·8768	0·8662	0·00635	0·00560
38·06	0·9085	0·8983	0·00868	0·00755
49·43	0·9406	0·9308	0·01256	0·01055
57·79	0·9642	0·9547	0·01688	0·01379
65·22	0·9851	0·9757	0·02358	0·01853
73·74	1·0090	0·9998	0·03670	0·02750
78·94	1·0237	1·0146	0·0495	0·0359
85·39	1·0420	1·0334	0·0748	0·0497
92·85	1·0623	1·0538	0·1193	0·0730
100·00	1·0836	1·0752	0·2010	0·1104

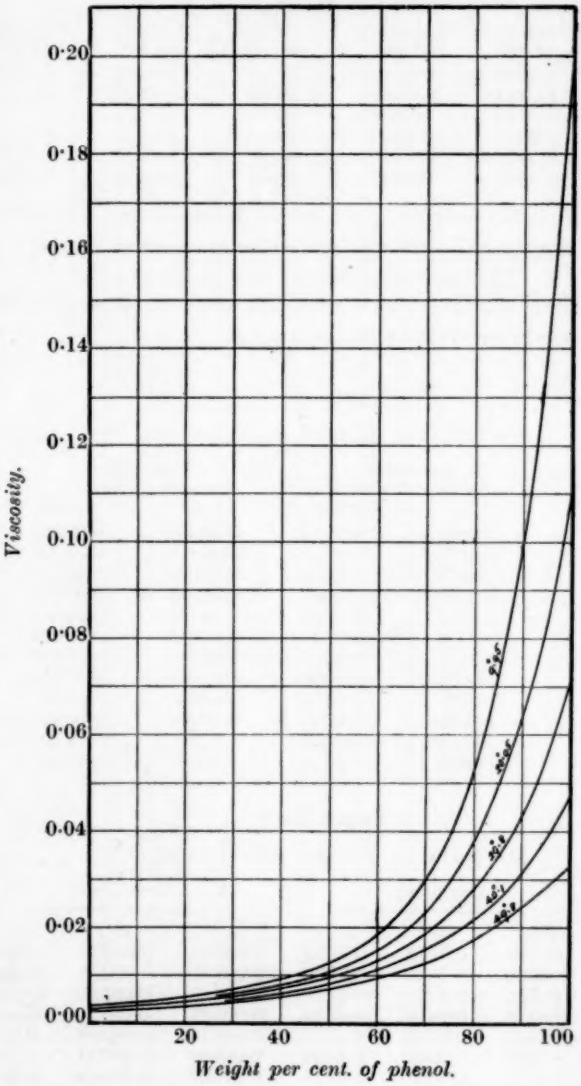
Table X*a*.

Mixtures of Phenol and Acetone.

Weight per cent. of phenol	Densities.			Viscosities		
	29·8°	40·1°	49·8°	29·8°	40·1°	49·8°
0·00	0·7799	0·7676	0·7559	0·00295	0·00270	0·00248
9·57	0·8056	0·7940	0·7830	0·00360	0·00328	0·00299
19·53	0·8336	0·8223	0·8116	0·00441	0·00399	0·00360
27·70	0·8572	0·8460	0·8335	0·00521	0·00470	0·00422
37·42	0·8855	0·8743	0·8636	0·00670	0·00590	0·00530
44·67	0·9063	0·8952	0·8846	0·00808	0·00711	0·00628
53·79	0·9330	0·9220	0·9115	0·01058	0·00904	0·00794
60·24	0·9520	0·9416	0·9316	0·01319	0·01101	0·00950
67·19	0·9724	0·9625	0·9530	0·01658	0·01363	0·01150
74·25	0·9935	0·9837	0·9733	0·02180	0·01741	0·01425
80·76	1·0115	1·0022	0·9933	0·02910	0·02230	0·01785
87·98	1·0327	1·0237	1·0150	0·03915	0·02875	0·02245
92·81	1·0466	1·0378	1·0293	0·04905	0·03465	0·02615
100·00	1·0668	1·0584	1·0503	0·07100	0·0474	0·0328

FIG. 10.

Phenol and acetone.



Discussion of Results.

A general survey of the work described in the foregoing pages leads to the following general conclusions:

(1) When a substance, such as phenol, which, in the liquid state,

consists largely of associated molecules, is mixed with another indifferent substance, such as benzene, chlorobenzene, or nitrobenzene, the viscosity of the mixture is considerably lower than that calculated according to the simple mixture rule. The viscosity-composition curve shows a very marked curvature, convex towards the axis of composition.

(2) When the formation of a compound takes place, as, for example, when phenol is mixed with such bases as aniline, *p*-toluidine, and quinoline, the viscosity of the mixture is, in general, higher than that calculated by the simple mixture rule. The viscosity-composition curve is concave towards the composition axis. That the high viscosity of these mixtures is caused by the acidic nature of phenol is shown clearly by displacing the hydroxyl hydrogen by an alkyl group, thus obtaining a neutral substance, phenetole, for example, which, with aniline, yields mixtures the viscosity curves of which are convex towards the axis of composition.

(3) The position of the maximum point on the viscosity curves generally varies with the temperature, and can, therefore, give little indication as to the composition of any compound that might be present. Further, in every case described in this paper, where there is a positive deviation, the composition of the mixture the viscosity of which shows a maximum positive deviation depends on the temperature at which the viscosities are measured; the nature of the relationship between these two quantities is indicated by the small curves inset in the various figures. This is altogether different from what Denison found. On examining these small curves, it will be seen that they are all convex towards the composition axis; they lie entirely on one side of the ordinate representing molecular proportions, and, if produced in the direction of higher temperatures, they would approach this ordinate asymptotically. These peculiarities are, in all probability, the result of an unequal thermal dissociation of the molecular complexes of phenol and of the compound formed, the opposing influence of these two kinds of molecular complexes being altered in favour of the compound. This is well illustrated by the mixtures of pyridine and phenol. At 10°, only a very small portion of the viscosity curve is concave towards the axis of composition. This curve resembles very closely the one for phenol and benzene, and, were it not for the slight inflexion near that end of the curve where the mixtures are rich in phenol, it might be taken as a typical case of a mixture of two indifferent substances, one of which contained associated molecules. Several unsuccessful attempts were made to measure the viscosity of phenol at 0° with the object of ascertaining whether the inflexion

of the viscosity curve would disappear at this temperature. With rise in temperature the part of the curve which is concave towards the composition axis becomes more pronounced, and above 40° a well defined maximum appears. The viscosity curve for this mixture at 10° has only about 15 per cent. of its length above the straight line joining the viscosities of the pure components, whereas at 110° there is only about the same proportion below the corresponding straight line. At the lower temperatures, the effect of the associated phenol molecules on the viscosity is predominant, whilst at the higher temperatures the influence of the pyridine–phenol complexes is more assertive. The development of a maximum on the viscosity curve of a mixture with rise in temperature appears to be rather unusual. Faust found the opposite effect with mixtures of ether and acetone.

The difference between the viscosity curves for mixtures of phenol with aniline and dimethylaniline may be accounted for by the weaker basic nature of the latter.

As regards the viscosity curves for mixtures of phenol with diphenylamine and diphenylmethylamine, it will be noticed that in neither case do the curves fall as far below the straight line joining the viscosities of the pure components as is the case for mixtures of phenol and benzene. Since there is no reason to suppose that either diphenylamine or diphenylmethylamine has a weaker dissociating action on the associated phenol molecules than has benzene, the smaller curvature of the viscosity curves for mixtures of phenol and these two very weak bases may be the result of the counteracting influence of compound-formation.

The viscosity curves for mixtures of phenol and acetone, unlike those of phenol and pyridine, show no change in character with rise in temperature. The associated phenol molecules are predominant throughout. It should be borne in mind, however, that the range of temperature over which this mixture has been examined is relatively small, and although, as has been shown by Schmidlin and Lang (*Ber.*, 1910, **43**, 2812), compound-formation certainly takes place. the amount of compound formed is undoubtedly much smaller than in the phenol–pyridine mixtures at the same temperatures.

A number of experiments on the influence of pressure on the viscosity of liquids have been made by Warburg and Sachs (*Ann. Physik.*, 1884, [iii], **22**, 518) and Cohen (*ibid.*, 1892, [iii], **45**, 666), who found that increase in pressure generally causes an increase in viscosity. This increase in viscosity may not be the direct result of the increase in pressure, but of the decrease in volume resulting from the latter. Cohen found that the change in viscosity is not

proportional to the increase in pressure. Bogojawlenski and Tammann (*Zeitsch. physikal. Chem.*, 1898, **27**, 457) investigated the relative effect of pressure on the viscosity and specific volume of water at 0°, and found that they are not proportional. That influences besides mere volume changes play a far more important part in determining the viscosity of a liquid is shown in a most striking manner by the results obtained in this investigation. In every case studied, the density-composition curves for the different temperatures run very nearly parallel; in no case is this so with the viscosity curves. A reference to the mixtures of phenol with quinoline and pyridine will illustrate this. The former of these two mixtures has a marked maximum on the density curves. The maximum increase in density, or the greatest contraction in volume produced by mixing, takes place at all temperatures when the mixture contains about 47 per cent. of phenol, and, further, the amount of this contraction is very approximately the same for every temperature studied. A glance at the viscosity curves in Fig. 8 will show how different these are. In the phenol–pyridine mixtures there is a maximum contraction in volume at 59 to 60 per cent. of phenol. In this case also, both the composition of the mixture which shows maximum contraction and the extent of this contraction are almost independent of temperature. Nothing could be more different than the viscosity curves for this mixture; not only is there a lack of parallelism, but they change in character from one extreme to the other with rise in temperature. If contraction in volume, resulting from whatever cause, were the dominant factor in increasing the viscosity, at least some approach to a proportional relative increase in viscosity and volume-contraction might be expected. Experiment shows that this is not the case.

I wish to express my sincere thanks to Professor Philip for placing the resources of his laboratory at my disposal, and for the kind interest he has taken in the work throughout.

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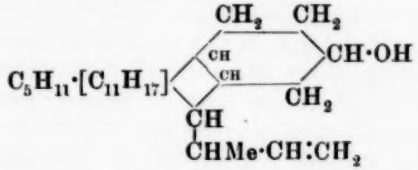
IV.—*Contributions to the Chemistry of Cholesterol and Coprosterol. Part III. The Ozonides of Cholesterol. Part IV. The Action of Bromine on Cholesteryl Benzoate.*

By CHARLES DORÉE and LIONEL ORANGE.

RECENT researches on the constitution of cholesterol may be summarised in the following formula:



In addition to the double linking situated in the end vinyl group, the possible presence of another, which must be placed in the complex $C_{11}H_{17}$, has been the subject of considerable discussion. The evidence rests almost entirely on the nature of the action of ozone on cholesterol, but in different hands this reagent has given very different results. In 1908 one of us first showed that whilst cholesterol formed an ozonide, $C_{27}H_{46}O{\cdot}O_3$, the corresponding ketone gave a compound, $C_{27}H_{44}O{\cdot}O_7$.

This number was in keeping with the views then held for the number of oxygen atoms which should combine with a doubly unsaturated ketone, and the statement was made that "it may be that cholestenone contains a second ethylene linking which is not rendered apparent by the usual reagents" (T.. 1908, **93**, 1330).

Langheld (*Ber.*, 1908, **41**, 1023) mentioned that cholesterol appears to combine with at least two ozone complexes. Diels, however, found that the crude ozonide, after treatment with alcohol, lost oxygen, and that a definite compound, $C_{27}H_{46}O,O_4$, resulted, for which he suggested a peroxide formula (*Ber.*, 1908, **41**, 2596). Molinari and Fenaroli obtained, in ethereal solution, products containing between 3 and 4 atoms of combined oxygen per molecule, but later, using ozonised air of 1 per cent. ozone concentration, they obtained ozonides, $C_{27}H_{46}O,O_6$, stable at 60°, from cholesterol and phytosterol. They stated that these results confirmed the existence of a second double linking in cholesterol, and further claimed that the increase in weight of an unsaturated compound after treatment with ozone, gave an 'ozone number' which was a measure of the number of ethylene linkings present

(*Ber.*, 1908, **41**, 2785). This method was extended by one of us to a series of derivatives of cholesterol (T., 1909, **95**, 638). Under prolonged action of the ozone stream cholesterol and cholestenone were found to combine with two molecular proportions of ozone. The saturated dihydrocholesterols, β-cholestanol and coprosterol, still gave ozonides, $C_{27}H_{48}O,O_3$, but the ketones corresponding with these showed an addition of O_6. This inconsistency has recently been criticised by von Fürth and Felsenreich (*Biochem. Zeitsch.*, 1915, **69**, 416), but it serves to show that the action of ozone is not as simple as was at first assumed. The behaviour of the dibasic acid, $C_{27}H_{44}O_4$ (Diels, *Ber.*, 1906, **36**, 3177) was also examined. It is insoluble in ordinary solvents, but the ozonides are readily soluble. At the solution point (six hours) an ozonide, $C_{27}H_{44}O_4,O_3$, formed by saturation of the characteristic double linking, was obtained; after one hundred hours a compound, $C_{27}H_{44}O_4,O_8$, was produced.

Harries (*Ber.*, 1912, **45**, 936; *Annalen*, 1912, **390**, 235) has brought evidence to show that the 16 per cent. ozone used by him contains two constituents, normal ozone, O_3, and oxozone, O_4, in the proportion $2O_3 : O_4$. If the crude ozone is passed through dilute sodium hydroxide solution, the oxozone is destroyed. This 'washed' ozone gives normal ozonides by the addition of O_3 for each unsaturated linking. The 'crude' ozone gives, not only the ozonide, X,O_3, and the oxozonide, X,O_4, but also polymerides of these $(XO_3)_2$ and $(XO_4)_2$. Further treatment with crude ozone leaves the normal ozonide unchanged, but the bisozonide is converted into the bisoxozonide.

These results may account for the varying compositions assigned to the cholesterol ozonides, but they do not seem to have been taken into account by von Fürth and Felsenreich, who, working with 8 per cent. ozone and using the ozone-number method with chloroform as a solvent, found that the molecule of cholesterol absorbs 1·5—4 molecules of ozone, dihydrocholesterol 1·8—4·3, and cholestane 1·5—4·8 molecules. They conclude that only one double linking exists in the cholesterol molecule. The ozonide results are, however, of little value. We have found that chloroform is strongly attacked by ozone, and that it is impossible to obtain a product free from chlorine when it is employed. Harries has found (*loc. cit.*) that cholesterol with washed ozone in hexane solution gives an ozonide, $C_{27}H_{46}O,O_3$, but in carbon tetrachloride solution an ozonide, $C_{27}H_{46}O,O_6$, is formed. The method of working, namely, evaporation of the solvent in the 8 per cent. ozone current and analysis of the crude residue obtained, does not seem very satisfactory. It has, moreover, lately been recognised that for the study of con-

stitution a weaker ozone of 1 to 2 per cent. concentration is desirable.

We have therefore made some preparations and analyses of the ozonides of cholesterol and of the acid $C_{27}H_{44}O_4$, in the hope of explaining some of these points, which are of importance both from the point of view of the constitution of cholesterol and of the nature of ozone action.

Experimental.

The ozonised oxygen used contained 2 per cent. of ozone. Passage through sulphuric acid did not alter the concentration, but after 'washing' through 5 per cent. sodium hydroxide it became 0·8 per cent. The cholesterol was ozonised in glacial acetic acid suspension, except in one or two cases. The acid $C_{27}H_{44}O_4$ was suspended in acetone. Acetic acid appears to be quite unaffected by ozone, and acetone is only slightly attacked. In order to form the ozonide $C_{27}H_{46}O{\cdot}O_3$, 1 gram of cholesterol requires 0·12 gram of ozone. Under the conditions of experiment this quantity was passed through per hour.

All the products obtained had very similar properties, and were worked up in the same way. The acetic acid solution was diluted with its own volume of light petroleum, and poured into twice the volume of water. The ozonide floated as a clot on the aqueous layer, and was easily removed. The aqueous layer was extracted with ether, the ethereal solution shaken with dilute alkali, and the ether evaporated. The total ozonide was dissolved in a little ether and precipitated with light petroleum, this process being several times repeated. The viscous clot obtained foamed in a high vacuum, and dried to a brittle solid which was easily powdered. It was kept for fourteen days in a vacuum before analysis. The acetone solutions were allowed to evaporate, and the ozonide treated as before.

The following tables give the theoretical composition of the various ozonides:

Table I.

Theoretical Composition of the Ozonides of Cholesterol, [H=1·008].

	$C_{27}H_{46}O$	$+O_3$	$+O_4$	$+O_5$	$+O_6$	$+O_7$	$+O_8$.
C	83·85	74·59	71·94	69·52	67·17	65·01	62·98
H.....	12·00	10·68	10·30	9·95	9·62	9·31	9·01

TABLE II.

Theoretical Composition of the Ozonides of the Acid $C_{27}H_{44}O_4$.

	$C_{27}H_{44}O_4$	$+O_3$	$+O_4$	$+O_5$	$+O_6$	$+O_7$	$+O_8$
C	74·95	67·45	65·32	63·28	61·36	59·55	57·85
H.....	10·26	9·23	8·87	8·44	8·19	8·09	7·85

The first series of experiments, table III, was made to discover whether cholesterol formed a higher ozonide than $C_{27}H_{46}O+O_3$, and, if so, what was the maximum number of oxygen atoms which could combine.

TABLE III.

The Extreme Action of Ozone on Cholesterol.

Expt.	Total time of treatment with ozone in hours.	Time in hours per 1 gram treated.	Ozone passed through	Rotation of ozonide. $[\alpha]_D^{18}$	Analysis C/H	Analysis indicates addition of
1.	16	3	H_2SO_4	+ 21°	66·66, 66·52 9·57, 9·55	O_6
2.	18	9	H_2SO_4	—	64·97, 65·56 9·21, 9·05	O_7
3.	21	10	—	21°	65·01, 65·27 8·93, 8·94	O_7
4.	60	24	NaOH + H_2SO_4	31°	67·35, 67·28 9·75, 9·83	O_6

Glacial acetic acid was used, except in experiment 1, which was in acetone solution. Rotations were measured in ethereal solution.

It being evident that a maximum of 6 or 7 atoms of oxygen could combine, attempts were made to ascertain the composition of the ozonide formed in the first stage of the action, that is, during the saturation of the double link in the terminal vinyl grouping. The results are given in table IV.

TABLE IV.

The Action of Ozone on Cholesterol in Glacial Acetic Acid Suspension, the experiments being stopped as soon as the cholesterol had passed into solution as ozonide.

Expt.	Total time of treatment in hours.	Time in hours per 1 gram treated.	Ozone passed through	Rotation of ozonide. $[\alpha]_D^{18}$	Analysis C/H.	Analysis indicates addition of
5.	8	2½	H_2SO_4	+ 35°	73·03, 72·33 10·49, 10·41	O_{3-4}
6.	5	2½	—	35°	71·11, 70·98 10·35, 10·10	O_4
7.	17	3	—	23°*	71·13, 71·21 10·63, 10·46	O_4
8.	3	1½	NaOH + H_2SO_4	—	74·89, 75·01 10·27, 10·86	O_{3-}
9.	10	4	NaOH + H_2SO_4	43°	73·38, 73·24 10·71, 10·64	O_{3+}

* Chloroform solution.

In so far as the solution point can be taken as indicating the end of the first stage, these results point to an addition of O_4 with crude ozone, and, with less certainty, of O_3 with normal ozone. The product obtained in experiment 8 was fully saturated towards bromine.

In the following experiments, 10—12, made with the acid $C_{27}H_{44}O_4$, the solution point was far sharper. In experiment 11 the action was stopped short of complete solution, and the excess of acid removed by filtration. Experiments 13 and 14 show the effect of prolonged treatment with crude and washed ozone respectively.

TABLE V.

Action of Ozone on the Acid $C_{27}H_{44}O_4$, *m. p.* 290°.

Expt.	Total time of treatment in hours.	Time in hours per 1 gram treated.	Ozone passed through	Rotation of ozonide. $[\alpha]_D^{18}$	Analysis C/H.	Analysis indicates addition of
10.	6	2	H_2SO_4	30°	64·45, 63·85 8·96, 8·83	O_{4-5}
11.	13	4	H_2SO_4	28°	65·03, 64·71 9·07, 9·08	O_4

TABLE V (*continued*).

Action of Ozone on the Acid $C_{27}H_{44}O_4$, *m. p.* 290°.

Expt.	Total time of treatment in hours.	Time in house per 1 gram treated.	Ozone passed through	Rotation of ozonide. $[\alpha]_D^{18}$	Analysis C/H.	Analysis indicates addition of
12.	8	4	NaOH + H_2SO_4	—	64·09, 64·20 8·91, 9·49	O_{4-5}
13.	25	8	H_2SO_4	13°	57·78, 57·66 7·55, 7·40	O_8
14.	33	20	NaOH + H_2SO_4	—	59·21, 59·74 8·00, 8·15	O_7

Statement and Discussion of Results.

(1) It will be seen that cholesterol combines with a maximum of seven atoms of oxygen under the action of ozone. With 'washed' or normal ozone the number is exactly six. The acid $C_{27}H_{44}O_4$ forms compounds, $[+O_7]$ and $[+O_8]$, on treatment with washed and crude ozone respectively.

(2) Experiments made to determine the first stage in the action point to the formation of an ozonide, $[+O_3]$, with cholesterol and washed ozone, but to an addition of O_4 in other cases.

(3) All the products obtained were brittle solids, which melted between 85° and 95°, and decomposed above 100°. Like other saturated cholesterol derivatives, they were dextrorotatory, the values for those made with washed ozone being higher than those made with crude ozone. No information was obtained by a study of their decomposition products, resinous acids and neutral substances being formed.

The formation of an ozonide, $C_{27}H_{46}O_7O_6$, as an end-product with ozone must, we think, be taken as evidence that a second double linking has entered into combination. The comparatively slow rate at which the reaction takes place leads to the conclusion that this linking does not exist pre-formed in the cholesterol molecule, but is developed under the action of ozone. Harries has suggested that water is eliminated from the grouping $\cdot CH(OH)\cdot CH_2\cdot$ with the formation of a cholesterylene, but this explanation scarcely holds in the case of the ketones and the acid $C_{27}H_{44}O_4$, which also form higher ozonides. The explanation previously given by one of us, that the secondary unsaturation is due to the opening up of a bridged ring under the influence of ozone, seems more probable, and has been adopted by von Fürth and Felsenreich. The analogies

of cholesterol with the terpenes render the presence of such a ring in the complex $C_{11}H_{17}$ by no means unlikely.

The ozonide $C_{27}H_{46}O,O_6$ must be formed by the addition of O_3 to an ozonide $C_{27}H_{46}O,O_3$, and experiments 8 and 9 point to this composition at the first stage of the action. The presence of oxozone, when crude ozone is used, tends to the production of compounds $[+O_4]$ and in each case such an ozonide is indicated by analysis. Prolonged treatment increases the proportion of oxozone combining, and explains the formation of ozonides $[+O_7]$ and $[+O_8]$.

We attempted to obtain some further evidence by the preparation of a cholesterol thio-ozonide.

Erdmann (*Annalen*, 1908, **362**, 133) put forward the view that the reactive, dark-coloured form of sulphur obtained by cooling the molten substance to 160° contains molecules S_3, and is the analogue of ozone. He found that it reacted with unsaturated organic compounds, forming thio-ozonides, especially with those containing a terminal vinyl group. Linalyl acetate, for example, gave a derivative, $C_{12}H_{20}O_2,S_3$, whatever the proportion of sulphur employed; linalool, instead of the expected $C_{10}H_{18}O,S_6$, gave a compound, $C_{10}H_{16}O,S_5$, with the evolution of hydrogen sulphide.

The following experiments were carried out with cholesterol:

(*a*) Ten grams were mixed with 3·5 grams of sulphur (S_3 requires 2·5) and heated at 160—165° for eight hours. Odour of hydrogen sulphide was not observed.

The dark red mass was dissolved in carbon disulphide, and the solvent allowed to evaporate. The uncombined sulphur crystallised out, and was separated by washing with cold benzene. Sulphur recovered, 1·1 grams; combined, 2·4 grams.

The compound was insoluble in alcohol, but moderately soluble in light petroleum, and very readily so in ether or benzene. It was purified by repeated precipitation with alcohol from benzene solution, and obtained as a dark red, brittle solid, melting indefinitely at 111°:

0·1264 gave 0·1957 $BaSO_4$. S = 21·2.

$C_{27}H_{46}OS_3$ requires S = 20·0 per cent.

(*b*) Several preparations were made, in which the proportion of sulphur and the method of purification were varied. The sulphur-content in each case was between 19 and 21 per cent. The substances proved extremely difficult to burn, and no satisfactory analyses could be obtained, the values found for carbon being 1—2 per cent. too low. For example, 10 grams of cholesterol were heated with 8 grams of sulphur, and the compound was purified by

fractional precipitation by alcohol from ethereal solution and extraction of the product with much boiling alcohol:

0·1654 gave 0·3947 CO_2 and 0·1291 H_2O. C = 65·1; H = 8·6.

0·2234 „ 0·3254 $BaSO_4$. S = 19·65.

$C_{27}H_{46}OS_3$ requires C = 67·2; H = 9·5; S = 20·0 per cent.

These analyses point to the formation of a compound having the composition of a thio-ozonide of cholesterol, and if Erdmann's assumptions are correct, they indicate that only one unsaturated linking capable of combining with sulphur is present in cholesterol.

Part IV.—The Action of Bromine on Cholesteryl Benzoate.

Obermüller (*Zeitsch. physiol. Chem.*, 1891, **15**, 42) observed that cholesteryl benzoate, when treated with bromine in carbon disulphide solution, gave a monobromo-substituted derivative,

$$C_{27}H_{44}OBr{\cdot}C_7H_5O$$

(m. p. 138°), instead of the expected cholesteryl benzoate dibromide. As the benzoate in this respect appears to differ from the other esters of cholesterol, we have repeated these experiments and extended them to the nitrobenzoyl esters.

An ethereal solution of cholesteryl benzoate was found to be indifferent towards bromine when treated with a solution of the reagent in glacial acetic acid. No absorption of bromine appeared to take place when the benzoate was dissolved in chloroform or carbon disulphide and treated at 0° with a solution of bromine in the same solvent, but in a few minutes the colour of the bromine disappeared, and thereafter it was instantly absorbed until the reaction was complete. Hydrogen bromide was evolved in small amount during and after treatment. Approximately 2 atoms of bromine were required per molecule of the benzoate. Two experiments showed (*a*) 3·35, (*b*) 3·45 grams of bromine per 10 grams of benzoate, whilst the absorption of 2 atoms of bromine requires 3·26 grams.

The crystalline product was very readily soluble in ether, chloroform, or benzene, sparingly so in light petroleum or acetone, and insoluble in alcohol. The microscope showed it to be a mixture which was resolved as follows: After crystallisation from a mixture of alcohol and chloroform, the mixture was crystallised from acetone. The first crops after washing with warm acetone consisted of soft needles melting at 138° (product A). The acetone filtrates, on keeping, deposited heavy, flat, hexagonal tablets, which were hard and gritty (product B). Shaking with light petroleum and repetition enabled them to be separated from the lighter masses of product A.

Product A was obtained in fine needles, which, when magnified, were seen to consist of narrow, six-sided prisms. These melted at 140—142°, and in other respects corresponded with the description of the monobromocholesteryl benzoate given by Obermüller.

Product B was purified by solution in acetone. On slow evaporation crystals more than 1 cm. in diameter could be obtained, which melted at 168—169°. The yield was not more than 20 per cent. of the total product:

0·1253 gave 0·2847 CO_2 and 0·0857 H_2O. C = 62·0; H = 7·7.
0·2819 required 8·76 c.c. $N/10$-$AgNO_3$. Br = 24·85.
$C_{34}H_{50}O_2Br_2$ requires C = 62·7; H = 7·8; Br = 24·6 per cent.

On treatment with zinc dust and acetic acid it was quantitatively reduced to cholesteryl benzoate. It would appear, therefore, to be the hitherto unknown *cholesteryl benzoate dibromide*.

Cholesteryl m-*nitrobenzoate*, $C_{34}H_{49}O_4N$, was prepared by heating together *m*-nitrobenzoyl chloride with cholesterol at 165° for five minutes. The product was almost insoluble in cold, more readily in boiling alcohol; sparingly soluble in acetone, and readily so in benzene or chloroform. After crystallisation from a mixture of alcohol and benzene the *m*-nitrobenzoate melted at 137° to a turbid liquid, which became clear at 170°. On cooling, a characteristic play of colours, violet, green, red, and orange, was observed.

Cholesteryl p-*nitrobenzoate* was also prepared, and closely resembled the *m*-compound. The crude product was extracted with alcohol, and the residue crystallised from acetone, and obtained in glistening plates, which melted at 185° (turbid liquid), decomposing at 250°. A play of colour, violet, green, and red, was here again observed.

On the addition of bromine to a solution of these esters in carbon disulphide solution an induction period was again noticed, after which absorption rapidly took place. Two atoms of bromine per molecule of the nitrobenzoate were required for complete reaction. Measurement of the hydrogen bromide evolved gave the following results:

One gram-molecule (535 grams) of cholesteryl *m*-nitrobenzoate required 159 grams (2 atoms) of bromine, of which 52 grams were evolved as hydrogen bromide. These numbers indicate a substitution of 52, and an addition of 55 grams of bromine, leaving some portion of the ester unaltered. Examination of the product confirmed this. A crystalline monobromo-derivative was separated in a yield of 20 per cent. of the theoretical. The residue consisted of a resinous mass, probably the impure dibromide, which could not be crystallised.

Bromocholesteryl m-*nitrobenzoate* was isolated from the crude

preparation by extraction with acetone. On recrystallisation from ethyl acetate it formed leaf-life crystals melting at 149°:

0·7624 gave 0·2423 AgBr. Br=13·5.

$C_{34}H_{48}O_4NBr$ requires Br=13·0 per cent.

From these results it would appear that it is the negative character of the benzoyl groupings that hinders the reactivity of the unsaturated linking. The acid $C_{27}H_{44}O_4$, in which this linking is also present, is quite indifferent towards bromine, although active towards ozone.

Summary.

(1) Evidence obtained from the action of ozone indicates that only one double linking exists in cholesterol.

(2) The secondary unsaturation shown by the existence of ozonides $C_{27}H_{46}O{\cdot}O_6$, is probably due to the opening up of a bridged ring.

(3) With sulphur, cholesterol yields a compound which approximates to the composition of a 'monothio-ozonide,' $C_{27}H_{46}O{\cdot}S_3$.

(4) The cholesteryl benzoates, unlike the other esters, form monobromo-substitution derivatives with bromine, as well as a dibromide.

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V.—*Studies in Catalysis. Part III. Preliminary Measurements of the Infra-red Absorption Spectra of Hydrogen Chloride, Potassium Chloride, and Methyl Acetate in Aqueous Solution.*

By Raphael Heber Callow, William Cudmore McCullagh Lewis, and Gerald Nodder.

In Parts I. and II. of this series (Lamble and Lewis, T., 1914, **105**, 2330; 1915, **107**, 233) it has been shown, on the assumption that homogeneous catalysis (such as the effect of acid on the inversion of sucrose and on the hydrolysis of methyl acetate) is due to the infra-red radiation emitted in quanta by the catalyst and absorbed

by the reacting substance, that the radiation from the hydrogen ion, and therefore the absorption bands possessed by it, should lie in the short infra-red region. Thus from measurements of the temperature-coefficient of the rate of inversion of sucrose by hydrogen chloride it was calculated that the characteristic frequency* of the hydrogen ion (neglecting any modification in numerical values which may be attributed to the effect of the solvent) should correspond with a wave-length of the order $1{\cdot}23\,\mu$, and similarly from the rate of hydrolysis of methyl acetate it was inferred that the position of the hydrogen-ion band should be $1{\cdot}9\,\mu$. The mean of these two values is $1{\cdot}56\,\mu$. From the results obtained by Coblentz ("Investigations of Infra-red Spectra," 7 parts, Pub. Carnegie Inst., 1905–1908) it is evident that radiation of this order of wave-length could be absorbed by sucrose and by methyl acetate, although the most marked bands of these substances occur at longer wave-lengths. These observations, however, refer to the substances in the pure state. No data are available as regards the position of the dissolved methyl acetate or hydrogen-ion bands, since neither ester nor strong acid has been examined in aqueous solution. It is of obvious importance for the radiation view of catalysis that such data should be obtained, and for this purpose the present investigation was carried out.

According to Coblentz (*loc. cit.*), the band at $3\,\mu$ in the water-transmission spectrum is due to the hydroxyl group, and the heavier the group the longer is the wave-length of the absorption band associated with it, for example, the SO_4 group gives rise to bands at $4{\cdot}55\,\mu$, $8{\cdot}7\,\mu$, and $9{\cdot}1\,\mu$. From this it would follow that if the hydrogen ion gave rise to any bands in the infra-red region, one or more of these should lie between $0{\cdot}8\,\mu$ and $3\,\mu$, provided the solvent itself did not mask or fundamentally modify the vibration of the solute. As a matter of fact, we have found that this modification takes place. The bands in the water spectrum in this region occur at: $0{,}77\,\mu$, $\mathbf{1{\cdot}0}\,\mu$, $1{\cdot}25\,\mu$, $\mathbf{1{\cdot}50}\,\mu$, $\mathbf{2{\cdot}0}\,\mu$, and $\mathbf{3{\cdot}0}\,\mu$, of which those in heavy type are the most prominent. In principle the present measurements consist in comparing the transmission of a layer of water with a layer of solution having the same thickness with respect to water, and isolating the effect of the solute by

* It is not implied that the hydrogen ion possesses only one band in the infra-red. From analogy to other substances it is probable that there are several bands, and further it is impossible at the present stage to attribute the catalytic activity to a single type of vibration. The term "characteristic frequency" might be called the "equivalent frequency," that is, the single frequency which would give rise to a single quantum of sufficient size to account quantatitively for the effects observed. Whether this is due actually to a single quantum or to more than one cannot at present be stated.

taking the water transmission value as unity at a series of wave-lengths.

Experimental.

The infra-red spectrometer employed was of the Hilger pattern with a range 0·5—10 μ. The source of radiation was a Nernst filament lamp (0·6 ampere and 190 volts), regulation of current being effected by means of a variable resistance. The beam of radiation is rendered parallel, and focussed by means of metallic mirrors, dispersion being obtained by means of a rock-salt prism, to which is attached a plane mirror to give automatically minimum deviation for all wave-lengths after a single setting. The telescope of the instrument is fitted for a thermopile to be used in conjunction with a galvanometer. Many attempts were made with different thermopiles used in conjunction with a Broca galvanometer to obtain readings, but owing to the lack of steadiness of the galvanometer zero, due to variable magnetic effects, the thermopile-galvanometer system had to be abandoned, and in its place a radiomicrometer was employed, which was found to give consistent readings. This instrument, which was constructed in the laboratory, was of the type recommended by H. C. Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 776). The suspended system consisted of a loop of pure silver wire supported on a glass frame and connected to a thermo-couple of the same kind as that employed by Jones. The compensating junction was found to nullify to a very large extent the disturbing influence of local variations in temperature due to the warming of the slit on exposure to the radiation. The radiation entered through a fluorite window, and was received on a thin plate of pure silver, blackened, and attached to the couple. The deflexion of the suspended system was observed on an illuminated scale by means of a reading telescope. In all cases it was found most advantageous to use the instrument ballistically, that is, to take the reading of the deflexion produced and completed in seven or eight seconds after raising the water-cooled shutter placed in front of the Nernst lamp.

The water and hydrogen chloride solutions were examined in quartz cells, two such cells being mounted on a horizontal carrier (placed directly in front of the collimator slit), so that the cells could be rapidly interchanged for comparative measurements. By means of stops it was possible to bring the cells to exactly the same position throughout a series of measurements in order that the amount of absorption due to the quartz walls would remain constant. The two cells most frequently employed were made by cementing quartz plates (each 1·5 mm. thick) on to the sides of a

thin U-shaped piece of glass with marine glue. The internal thickness of each cell was approximately 0·9 mm.

Sensitivity of the Radiomicrometer.—Sensitivity is defined as the deflexion in cm. per sq. mm. of exposed surface for a standard candle and scale each at a distance of 1 metre. The candle and scale were set up at this distance from the instrument, and the deflexion observed. Seven concordant readings gave as a mean value 6·0 cm. The width of the slit was 0·5 mm., and the area of exposed vane 1·5 mm.^{2}. Hence the sensitivity is 4·0. In this measurement the instrument was exhausted to a pressure of 2—3 mm. Jones (*loc. cit.*) obtained a sensitivity of 5 with his instrument under the ordinary pressure. Our instrument in its present form is therefore less sensitive, but has the advantage of possessing a very short period.

Change in Sensitivity with Time.—Before taking any set of readings, the deflexion with the spectrometer drum set at 2 μ was in all cases noted, the width of the slit of the radiomicrometer being permanently adjusted to 0·5 mm., and an empty quartz cell being placed in position in front of the collimator. The deflexion remained the same for several days, the maximum variation for widely separated intervals of time being from 161 to 155 mm. divisions on the scale. All values were reduced where necessary to the 161 mm. deflexion as standard.

Drum Calibration.—The position of the sodium-yellow and potassium-red lines indicated that the drum was correct for wavelengths shorter than 0·8 μ approximately. It was also found that the quartz band occurred at 2·9 μ, as Coblentz had observed, and that the water bands at 3·0 μ and 4·7 μ were correctly registered. Instead of obtaining the water band at 1·5 μ, however, the drum reading was 1·45 μ. This relatively small error in calibration has been allowed for in the data quoted later.

Percentage Error in the Deflexion Readings.—The region investigated extended approximately from 0·9 μ to 2·1 μ. At each point at least six independent readings were taken, and the experimental error thus obtained. For deflexions greater than 200 mm. the error is negligible. For smaller deflexions the average percentage error is as follows:

Deflexion in mm.	150	100	50	25	10	5
Per cent. error	±1·0	±1·25	±2·0	±4·0	±6	±10

Comparison of the Transmission of the Quartz Cells.

Readings were taken through each cell when empty. Over the range investigated no measurable difference could be detected. When the cells were filled with water, differences were observed,

due to the difference in thickness of the water layers. A table of values was constructed, from which observations made on one cell could be reduced to that of the other. This correction will be referred to as the "correction for the dimensions" of the cell.

Infra-red Absorption of Hydrogen Chloride in Aqueous Solution.

The acid was investigated at three concentrations, namely, N, $2N$, and $3N$. The solution was placed in one of the cells (A), water in the other (B), and readings taken alternately through each. In order that the deflexions may be comparable, it is necessary to correct for the displacement of water by the acid in the solutions. This was effected by determining the absorption-coefficient, k, of water. One of the cells was made considerably thinner than the other, the difference being 0·55 mm. The law of absorption is expressed thus:

$$I = I_0 e^{-kd},$$

where I_0 is the intensity of the incident radiation, I the intensity of the emergent beam, and d the thickness of the water-layer traversed. Knowing the thickness of the two cells exposed to the same intensity, I_0, it is possible to calculate k for water at various wave-lengths. In this way a table of values was prepared, the unit of length being the millimetre. Returning to the comparison of cells A and B, when the solution in A was compared with the water in B it was possible from a knowledge of the density of the solution to determine the effective thickness of water actually traversed; knowing k, it was then possible to alter the values of the deflexion observed through cell B to the values which would have been given if the beam had traversed in B the same thickness of water as exists in cell A. This was the general method of correction adopted, and will be referred to as the "correction for density." A single illustration of the method may be given in the case of N-hydrochloric acid. The density of this solution is 1·017. The concentration of hydrogen chloride is 0·0365 gram per c.c., and hence the concentration of water (in cell A, containing the solute) is 0·9805 gram per c.c. The concentration of water in cell B is taken as unity. Hence,

$$\frac{\text{Effective thickness of water in } A}{\text{Thickness of water in } B} = \frac{0\,9805}{1}.$$

The actual thickness of the water-layer in B is 0·92 mm. Hence the effective thickness of water in A is 0·90 mm. The intensity, I, of the emergent beam from cell B thus requires to be increased to the value it would have (I') if the cell were 0·90 mm. thick. It is evident that $I' = Ie^{k(0\cdot92-0\cdot90)} = Ie^{0\cdot02k}$. With the aid of the known

value of k one can thus calculate I' from the observed value I. On dividing the deflexion through the acid solution by that through the water (corrected) at the same wave-length, the absorption due to the acid alone can be determined. The following table (I) contains in full the results obtained, and the extent of the corrections in the case of N-hydrochloric acid. The remaining tables do not contain the corrections, the final corrected results only being given.

TABLE I.

N-Hydrochloric Acid.

Wave-length in μ.	Deflexion through acid solution (cell A).	Deflexion observed through water (cell B).	Deflexion through B corrected for dimensions.	Deflexion through B corrected for density.	Deflexion in A / corrected deflexion in B.
1·0	40·0 mm.	39·3 mm.	38·5 mm.	38·6 mm.	1·04
1·12	67·0	63·5	65·4	65·6	1·02
1·23	82·0	78·8	80·4	80·8	1·01
1·34	66·0	62·0	65·1	65·7	1·00
1·45	84·5	78·5	84·8	85·8	0·98
1·50	99·0	95·5	104·1	106·4	0·93
1·55	109·0	105·5	117·1	119·6	0·91
1·65	96·8	95·5	102·2	104·0	0·93
1·74	66·6	68·0	75·5	76·9	0·86
1·84	42·0	45·1	50·1	51·1	0·82
1·93	34·9	34·6	40·1	41·3	0·86
2·03	30·3	29·9	35·9	37·2	0·81
2·13	23·0	23·6	30·0	31·4	0·73

The last column gives the fractional absorption exerted by the solute.

TABLE II.

2N-*Hydrochloric Acid.*

Wave-length in μ.	Deflexion through acid solution (cell A).	Deflexion through water (corrected) (cell B).	Deflexion in A / deflexion in B.
1·0	42·8 mm.	41·5 mm.	1·03
1·12	69·8	69·8	1·00
1·23	84·6	82·8	1·02
1·34	70·7	71·3	0·99
1·45	83·5	89·5	0·93
1·50	92·5	105·4	0·87
1·55	96·0	114·4	0·84
1·65	85·4	99·1	0·86
1·74	64·5	79·3	0·81
1·84	43·2	57·0	0·76
1·93	32·2	45·8	0·70
2·03	23·3	38·8	0·60
2·13	21·0	32·3	0·65

TABLE III.

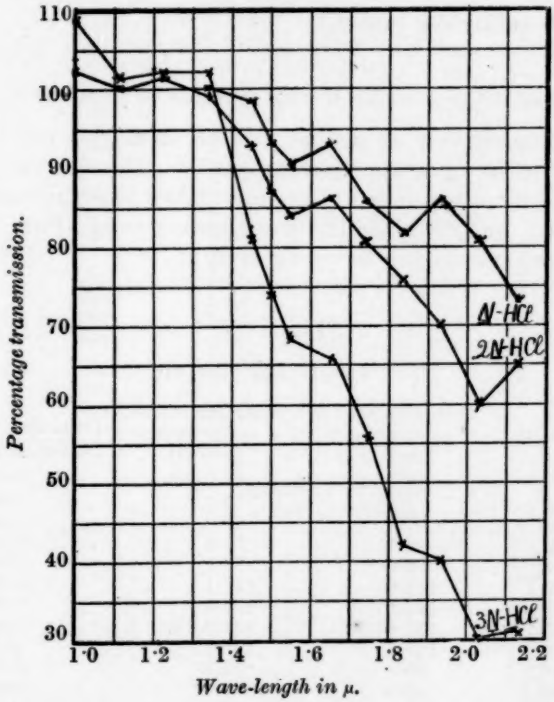
3N-*Hydrochloric Acid.*

Wave-length in μ.	Deflexion through acid solution (cell A).	Deflexion through water (corrected) (cell B).	Deflexion in A / deflexion in B.
1·0	39·5 mm.	36·3 mm.	1·09
1·12	66·0	64·8	1·02
1·23	83·0	80·3	1·03
1·34	66·0	63·9	1·03
1·45	69·0	83·4	0·81
1·50	77·0	104·0	0·74
1·55	79·5	116·8	0·68
1·65	68·1	103·0	0·66
1·74	41·4	73·7	0·56
1·84	25·2	60·0	0·42
1·93	16·0	40·6	0·40
2·03	11·0	37·4	0·30
2·13	10·0	31·9	0·31

The data of tables I—III are shown graphically in Fig. 1. It is evident that hydrogen chloride in aqueous solution exhibits

considerable absorption in the short infra-red region. As far as this goes, it supports qualitatively the conclusion already drawn as regards the effect of the acid in increasing the radiation density in this region. At the shorter wave end of the region examined the solution is actually more transparent than water. This phenomenon has been observed by others, and must be attributed to a change in the nature, and therefore in the absorbing power of a certain fraction of the water molecules, brought about by the presence of the dissolved substance. This may mean either that the

FIG. 1.



solute has become hydrated, the water of hydration being physically different from water in the uncombined state, or the presence of the solute may have altered the position of equilibrium obtaining between the various polymerised forms of water, and have thus altered the absorption power. The most important conclusion, however, which can be drawn from the data obtained has to do with the positions and relative intensities of the bands of the acid. There appear to be at least three bands in this region, namely, a weak one at 1·12 μ, a stronger band at 1·55 μ, and one still stronger

in the neighbourhood of 2·1 μ.* The resemblance of these bands in respect of position and intensity to the bands exhibited by water itself, namely, 1·0 μ, 1·5 μ, and 2·0 μ, is so remarkable that it is fairly evident that the solvent has exerted a very marked effect on the type of vibration possessed by the solute. In view of this apparent effect it is necessary to examine the behaviour of other substances dissolved in water. For the sake of comparison, methyl acetate was therefore investigated in aqueous solution as being a substance totally unlike hydrogen chloride in respect of chemical constitution, and yet catalysable by the acid, and, further, potassium chloride was examined as being similar to hydrogen chloride, yet lacking its catalysing power.

Infra-red Absorption of Methyl Acetate in Aqueous Solution.

The concentration of methyl acetate employed was 10 c.c. in 50 c.c. of solution, or approximately 2·6*N*. This concentration was chosen as it corresponded with one of the cases investigated by Mr. Griffith, and described in the succeeding paper (Part IV). The results are given in the following table:

TABLE IV.

2·6N-*Methyl Acetate.*

Wave-length in μ.	Deflexion through ester solution (cell *A*).	Deflexion through water (corr.) (cell *B*).	Deflexion through *A*. / Deflexion through *B*.
1·0	43·2 mm.	42·1 mm.	1·03
1·12	71·3	73·2	0·96
1·23	97·3	96·6	1·00
1·34	82·5	79·3	1·04
1·45	96·6	92·1	1·05
1·50	119·0	127·1	0·93
1·55	133·5	144·4	0·92
1·65	132·8	137·9	0·96
1·74	101·7	105·2	0·97
1·84	68·4	71·4	0·95
1·93	52·3	61·0	0·86
2·03	40·8	53·2	0·77
2·13	34·5	51·6	0·67

These data are shown by one of the curves in Fig. 2. It will be observed that the ester exerts considerably less absorption than hydrogen chloride at the same concentration. Again, however, bands appear at 1·12 μ, 1·55 μ, and another beyond 2·1 μ. Coblentz (*loc. cit.*) has examined the pure substance from the wave-length 1·7 μ approximately, at which point the fractional absorption was

* Gaseous hydrogen chloride has, according to Ångstrom and Palmer, an emission band at 3·98 μ.

0·81, a feeble band manifesting itself at 2·2—2·4 μ, and a very marked band at 3·3 μ.

Infra-red Absorption of Potassium Chloride in Aqueous Solution.

The solutions examined were respectively N, $2N$, and $3N$. The results are given in the following tables:

TABLE V

N-Potassium Chloride.

Wave-length in μ.	Deflexion through solution (cell *A*).	Deflexion through water (corrected) (cell *B*).	Deflexion in *A* / Deflexion in *B*.
1·0	38·0 mm.	34·9 mm.	1·09
1·12	62·0	61·0	1·01
1·23	75·0	72·7	1·03
1·34	68·0	62·8	1·08
1·45	99·0	97·2	1·02
1·50	121·0	114·8	1·05
1·55	124·0	126·9	0·98
1·65	108·0	104·5	1·03
1·74	74·0	74·7	0·99
1·84	56·0	53·3	1·05
1·93	46·5	45·8	1·01
2·03	41·0	39·8	1·03
2·13	32·0	35·9	0·89

TABLE VI.

2N-Potassium Chloride.

Deflexion through solution (cell *A*).	Deflexion through water (corrected) (cell *B*).	Deflexion in *A* / Deflexion in *B*.
39 mm.	37·0 mm.	1·05
64	63·0	1·01
81	80·0	1·01
67	64·0	1·05
92	85·5	1·07
111	113·0	0·98
122	127·0	0·96
109	108·0	1·00
77	79·5	0·97
54	54·0	1·00
43	47·4	0·91
37	42·0	0·88
30	36·5	0·82

TABLE VII.

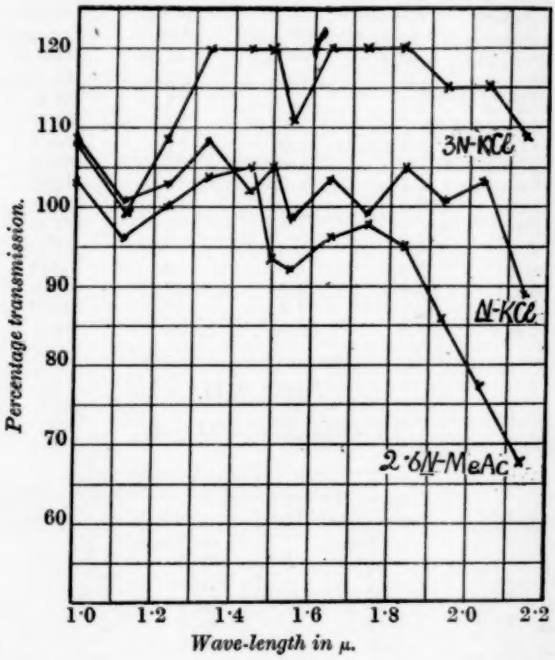
3N-Potassium Chloride.

Wave-length in μ.	Deflexion through solution (cell *A*).	Deflexion through water (corrected) (cell *B*).	Deflexion in *A* / Deflexion in *B*.
1·0	37 mm.	34·3 mm.	1·08
1·12	61	61·8	0·99
1·23	74	73·4	1·08
1·34	75	63·0	1·20
1·45	110	91·8	1·20
1·50	131	109·0	1·20
1·55	138	124·0	1·11
1·65	121	99·5	1·20
1·74	85	71·0	1·20
1·84	61	51·0	1·20
1·93	51	44·5	1·15
2·03	45	39·6	1·15
2·13	35	33·0	1·08

These data are given in Fig. 2. It is evident that potassium chloride exerts very little absorption compared with hydrogen chloride. It can, therefore, only slightly affect the radiation density of the system, and its transparency would even lead one to expect that its behaviour should be the reverse of hydrogen chloride. Since

the latter is a strong catalyst, one would anticipate, therefore, on the radiation view, that potassium chloride would exert no positive catalytic effect, and might even be a feeble negative catalyst. So far as absence of effect is concerned at the ordinary temperature experiment bears out this conclusion. It will be observed that the 3*N*-solution of potassium chloride is more transparent than those more dilute, but that there is a reversal of the relative positions of the *N*- and 2*N*-solutions. Whether this has any considerable significance cannot be determined at present, for in those cases in which the transmission of the solution lies in the region of 100 per

FIG. 2.



cent. a small experimental error would unduly displace the curve. The contrast in behaviour of potassium and hydrogen chlorides is, however, unmistakable. As in the case of the other solutes, the curves for potassium chloride show apparent bands at 1·12 μ, 1·55 μ, and increasing absorption beyond 2·1 μ. There is also evidence of an extra band at 1·93 μ.

Discussion of Results.

Owing to the influence of the solvent on the mode of vibration of the solute it is not possible at this stage to attribute any of the

bands observed in the case of hydrochloric acid over the region investigated to hydrogen ion as distinct from the acid as a whole. What has been shown, however, is that hydrogen chloride possesses certain well-marked bands in the short-wave region, and, further, in contrast with the behaviour of potassium chloride, the extent of absorption increases with the concentration. So far as position of bands is concerned, hydrogen chloride is capable of functioning as a catalyst in the sense of the radiation hypothesis already advanced, although it cannot be stated that the catalytic effect may be attributed to one band only. Having drawn attention to the contrast between the behaviour of hydrogen chloride and potassium chloride, it is at the same time important to point out the striking similarity in their curves in respect of the position of the bands. These occur at the same places (within the limit of experimental error), namely, at slightly longer wave-lengths than the bands of water itself. The solvent has produced forced vibration of similar type in both these solutes, and in methyl acetate as well. Coblentz (*loc. cit.*) had previously investigated a few solutions in the infra-red down to 5 μ, the solvent being carbon tetrachloride, and the solutes being respectively diphenyl, naphthalene, and azobenzene. Coblentz concludes that these substances absorb infra-red radiation, and further, "that the selective absorption of a solid in solution and that of the solvent are identical." According to the results obtained in aqueous solution it would appear that Coblentz's conclusion is not accurately true in all cases, and this is further emphasised by the fact that "solvent" and "solute" are ultimately interchangeable terms. From the present data, and also from Coblentz's curves, it is apparent that the intensity of a given band is the determining factor. Thus carbon tetrachloride has two bands, at 3·0 μ and 4·5 μ respectively, of which the 3 μ band is slightly the stronger. Diphenyl itself possesses one marked band at 3·25 μ, whilst the solution of diphenyl exhibits two bands, one at 3·25 μ and the other at 4·45 μ approximately. It appears, therefore, that the strong diphenyl band (at 3·25 μ) has masked the solvent band which should have manifested itself at 3·0 μ, whilst the solvent band at 4·5μ persists in the solution (with slight displacement), since the solute alone has no band at this point. It is immaterial whether one of the substances is the solvent, except in so far as the concentration of the solvent is usually large, and intensifies its own bands. The results with naphthalene are the same, the strong naphthalene band at 3·25 μ being the only one that appears in that region even when naphthalene is in the dissolved state, whilst a second band appears at 4·45 μ, due to the solvent. In the case of water which is characterised by intense

absorption, it may be inferred that solutions containing this solvent will exhibit the solvent bands (slightly displaced), and this, too, when the absorption of the solvent has already been allowed for. This point of view brings Coblentz's observations into line with our own.

We have finally to consider what mechanism underlies this masking effect produced by strong bands. The simplest view is to ascribe the phenomenon to general solvation, the solvated (hydrated) compound produced possessing the most intense bands of both its constituents, and exhibiting these at slightly displaced positions, the displacement being due to the change in the electromagnetic friction term denoted by "g" on the Lorentz notation. As a particular case, therefore, it would be inferred that when methyl acetate is dissolved in water at least one additive compound is produced, although not necessarily in large quantity. It is significant that the bands of the supposed additive compound occur just on the long-wave side of the bands exhibited by the solvent alone. On the basis of the electromagnetic theory of radiation it is known that the radiation density is abnormally high for the wave-length region just below a band. This means that the additive compound exists in a medium for which the radiation density is high just at the wave-lengths which the complex can most readily absorb. On the radiation view of chemical reactivity put forward in the previous communications, it may be anticipated that this compound in the presence of excess of water is chemically activated, and therefore tends to decompose into its two constituents, ester and water. Although water is necessary for the production of the compound in a stoicheiometric sense, its presence in excess is harmful in a catalytic-radiation sense. In other words, water acts as a negative catalyst, and the amount of compound formed will not be in strict accordance with the principle of mass-action. This conclusion from the radiation hypothesis—which would appear to be a general one—bears very directly on the results obtained in the case of the hydrolysis of methyl acetate, described in the succeeding paper (Part IV).

Summary.

(1) Employing a radiomicrometer of the H. C. Jones type, the infra-red absorption spectra of hydrogen chloride, potassium chloride, and methyl acetate in aqueous solution have been examined over the range 1 μ—2·1 μ.

(2) These solutes exhibit remarkably similar behaviour in respect of the position of the absorption bands which occur at 1·12 μ, 1·55 μ, and 2·1 μ (approx.), and thus correspond with the bands of

water itself with a slight displacement in each case in the direction of longer wave-length.

(3) It is suggested that the behaviour observed is due to the formation of additive compounds between the solute and the solvent.

(4) It is shown that hydrogen chloride possesses much greater absorptive power in the short infra-red region than does potassium chloride. This is in agreement with the radiation theory of homogeneous catalysis, according to which a positive catalyst is one which increases the radiation density at certain parts of the short infra-red region, and it is well known that the existence of an absorption band increases the radiation density abnormally for wave-lengths below the band, and diminishes it for wave-lengths above the band.

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VI.—*Studies in Catalysis. Part IV. Stoicheiometric and Catalytic Effects Due to the Progressive Displacement of one Reactant by Another in the "Acid" Hydrolysis of Methyl Acetate.*

By ROBERT OWEN GRIFFITH and WILLIAM CUDMORE MCCULLAGH LEWIS.

IT is a remarkable fact, although it does not appear to have attracted as much attention as it deserves, that the velocity-constant k for the reaction

$$CH_3{\cdot}CO_2{\cdot}CH_3 + H_2O \longrightarrow CH_3{\cdot}OH + CH_3{\cdot}CO_2H,$$

as obtained from the equation $k = \frac{1}{t}\log\frac{a}{a-x}$ varies with the initial concentration of the methyl acetate. Ostwald, who first investigated the reaction, obtained the following results (*J. pr. Chem.*, 1883, [ii], **28**, 449). At the temperature of 25·2°, with the same concentration of hydrochloric acid in each case ($2N/3$), the concentrations of ester employed in the experiments were 2 c.c., 1 c.c., 0·5 c.c., and 0·3 c.c. respectively in 15 c.c. of solution.

With 2 c.c. of methyl acetate, $k = 24{\cdot}19$.
" 1 " " " $k = 21{\cdot}96$.
" 0·5 " " " $k = 20{\cdot}71$.
" 0·3 " " " $k = 19{\cdot}91$.

Ostwald attributes this decrease in the velocity-constants to the fact that the end condition (in each case attained after two days) varies with the initial concentration in such a way that in the solution intially containing least ester the decomposition progresses to the furthest extent, and thus the velocity-constants differ because of the existence of an equilibrium point. He illustrates this in the following way. If we take in each case the final titration value in c.c. of alkali and subtract the value due to the hydrochloric acid, we obtain the value due to the acetic acid formed by the hydrolysis of the ester. Dividing these figures by the initial amount of ester in c.c. in each experiment, one would expect the same value if the total amount or some fraction of the ester were decomposed in each case. The table given below shows, however, that this is not so.

TABLE I.

Initial ester in c.c.	End point in c.c. of barium hydroxide solution.	C.c. of barium hydroxide solution required for 1 c.c. of ester.
2·0	25·96	12·98
1·0	14·34	14·34
0·5	7·66	15·32
0·3	4·66	15·53

Ostwald states that the magnitudes given in the last column of table I. and the corresponding velocity-constants are inversely proportional. A fairly constant result is obtained by multiplying the figures in the last column by the corresponding velocity-constants. From this he deduces the empirical relation which should hold for all different initial concentrations of ester, namely,

$$\log \frac{a}{a-x} = k\frac{a}{\beta}t.$$

in which β is the initial concentration of ester and a, x, and t have their usual significance. This relation holds independently of the nature of the acid.

In criticising this result, the first point to be noted is that the constants are not truly comparable as they stand, for the concentration of the water differs in each experiment, and the reaction-velocity should be proportional to the concentration of the water. In the experiments with the largest amounts of methyl acetate there is less water than in the others. This obvious correction, which was applied by Rosanoff to the case of the inversion of sucrose (*J. Amer. Chem. Soc.*, 1913, **35**, 248), has the effect of making the constants diverge still more from each other. This correction, which we will call the "stoicheiometric" correction for water, can be very approximately applied to Ostwald's results by

assuming that the methyl acetate displaces its own volume of water from the solution. In this way we obtain the following.

TABLE II.

Ostwald's unimolecular constants.	Constants corrected for variation in water content.
24·19	1·888
21·96	1·590
20·71	1·447
19·99	1·378

The corrected constants are obtained by dividing those of Ostwald by the weight of water present in 15 c.c., the total volume of solution in Ostwald's experiments. As the figures are purely relative, the above method serves for comparison. From the tables given above, it is seen that the divergence is now greater than before, so that Ostwald's empirical relation loses much of its significance. In order, therefore, to attempt to determine satisfactorily whether the change in the velocity-constant is due to the variation in the end point, that is, the equilibrium point, with different initial concentrations of the ester, the present research was undertaken.

The Accurate Velocity Equation.

The reaction is obviously bimolecular and reversible, although in dilute aqueous solution a unimolecular constant is necessarily obtained.

Denoting the initial concentration of the methyl acetate in mols. per litre by b, the number of mols. decomposed at time t by x, and the concentration of the water in mols. per litre by w, the velocity-constant for the decomposition of the ester by k_1 and the velocity-constant for the formation of ester by k_2, we have the differential equation

$$\frac{dx}{dt} = k_1(b-x)(w-x) - k_2x^2.$$

Writing $\frac{k_2}{k_1} = K$, the equilibrium constant, where

$$K = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acetic acid}]},$$

and also setting $y = w + b$ and $A = \sqrt{(w+b)^2 + 4(K-1)wb}$, integration gives, remembering that when $t = 0$ $x = 0$,

$$k_1 = \frac{1}{tA} \log. \frac{A + y + 2(K-1)x}{A - y - 2(K-1)x} \cdot \frac{A+y}{A-y} \quad . \quad . \quad . \quad (1)$$

and

$$k_2 = Kk_1$$

As is to be expected, neglect of the change in the concentration of water during an experiment makes very little difference in the value of k_1 obtained.

Assuming that w is a constant, we have

$$\frac{dx}{dt} = k_1 w(b - x) - k_2 x^2.$$

This on integration gives a value for k_1 which is very near to the value obtained as above (generally within 1 per cent.), although the variation in the concentration of water from beginning to end of a reaction is, in the case of the most concentrated solution of ester employed, more than 4 per cent. of the initial concentration of water. The more complete equation given above has, however, been employed throughout.

Experimental.

Methyl acetate was redistilled, and the portion boiling between 55·4° and 56·0° was used; it contained very little free acetic acid, the specific conductivity of an approximately normal solution of the ester in water being 40×10^{-6} mho. The concentration of the catalyst, hydrochloric acid, was $N/2$ in the first set of measurements, N in the second, and $N/10$ in the third. The concentrations of ester were respectively about 8, 5, 3, 1, and 0·5 c.c. in 50 c.c. of total solution. The exact concentrations in mols. per litre are given in the table of results. For the measurements of velocity, the usual method due to Ostwald was employed. The reactions were carried out in Jena-glass flasks which had been thoroughly steamed out and fitted with well-paraffined corks, the flasks being kept in a thermostat maintained at a constant temperature. From time to time a convenient volume of the reaction mixture was withdrawn by a pipette, run into 40 c.c. of conductivity water, and titrated against standard baryta. For each experiment two determinations were made, and the means of the two titres at corresponding times were taken to calculate the velocity-constants. The end points were taken after allowing the reaction to proceed for a time sufficient for equilibrium to be attained.

Before starting each experiment, the required amount of stock acid solution was run into the flask, together with that amount of water (previously determined) which with the ester gave a total volume of 50 c.c. This was then placed in the thermostat for thirty minutes, and the required amount of ester added at a noted time. Thus for each experiment the concentration of each constituent was known.

Determination of the Equilibrium Constant of the Reaction.

To determine K, the equilibrium-constant, a knowledge is required of the initial concentration of ester, the final concentration of the acetic acid, and that of the water. The final concentration of the acetic acid, which is identical with that of the methyl alcohol, is arrived at from the end-point titre obtained after ten times the time of half decomposition of the ester has elapsed, by which time the system is not appreciably removed from its condition of equilibrium. The initial concentration of the ester was not determined by weighing into a certain volume, but by treating the exact amount taken with an excess of baryta solution and then titrating with hydrochloric acid. The ester was treated with an excess of standard baryta solution for eight hours, precautions being taken to prevent entry of carbon dioxide from the air, and then the excess of baryta was determined. The difference between the initial concentration of ester and the amount decomposed after the solution had reached its position of equilibrium gives the amount of ester present at equilibrium, those of the methyl alcohol and acetic acid being, of course, equal to that of the decomposed methyl acetate.

The equilibrium-constant was determined only in the case of the two more concentrated solutions of methyl acetate, as experimental errors are magnified largely in calculating K for more dilute solutions, owing to the very large excess of one of the reactants—water. There is no reason, however, to believe that there is any variation in the equilibrium-constant with change in the concentration of the ester.

The following values were obtained for the equilibrium-constant

$$K = \frac{\text{ester} \times \text{water}}{\text{methyl alcohol} \times \text{acetic acid}}.$$

(1) In the presence of $N/2$-hydrochloric acid: 4·30, 4·52, 4·66, 4·80; (2) in the presence of $N/10$-hydrochloric acid: 4·52; and (3) in the presence of N-hydrochloric acid: 4·34, 4·83.

These are constant within experimental error, and the mean value 4·6 was adopted.

It may be noted, however, that the absolute value of K is not of great importance for the object of this research, as a fairly large variation in K makes but a small change in the value of the velocity-constant k_1 (constant for ester decomposition), although, of course, from formula (1) the value of k_2 is directly proportional to K. The equilibrium-constant K has been determined for the pure substances, with no added catalyst, by Berthelot and Pean de

St. Gilles (*Ann. chim. Phys.*, 1863, [iii], **68**, 225), who found that, starting with equivalent amounts of acetic acid and methyl alcohol, 67·5 per cent. of each combined. This gives $K=4{\cdot}31$. Further, Menschutkin (*Annalen*, 1879, **195**, 334) obtained 69·5 per cent. of combination, which gives $K=5{\cdot}18$.

The value 4·6 obtained above lies between the two. Now Lapworth and Jones (T., 1911, **99**, 1427) have shown that for ethyl acetate the presence of concentrated hydrochloric acid affects the value of K, which increases with decreasing values of the ratio H_2O/HCl. However, they found that, provided the concentration of the hydrochloric acid is below normal, the equilibrium-constant is very nearly independent of the hydrochloric acid present. Assuming that, in this respect, methyl acetate acts similarly to ethyl acetate, it is likely that no very sensible change in the value of K is to be expected in these experiments. The equilibrium-constant for this reaction in the presence of hydrochloric acid has also been determined by Worley (*Proc. Roy. Soc.*, 1912, [*A*], **87**, 582), who deduces, by extrapolation, the value $K=6{\cdot}6$ for the constant with no added catalyst present, a value decidedly higher than those obtained above.

Velocity Measurements.

Below are given the experimental results.
The following is the notation used:

t = time in minutes from the start.
x = number of gram-molecules of ester decomposed at time t.
k = unimolecular constant, $\frac{1}{t}\log_e\frac{a}{a-x}$.
k_1 = velocity-constant for ester decomposition
k_2 = velocity-constant for ester formation
} from equation (1)

Tables III. and IV. serve as an indication of the general character of the velocity-constants obtained in these experiments, whilst tables V. to VII. summarise the results of the experiments with hydrochloric acid as catalyst.

Table III.

Hydrolysis of methyl acetate with 0·5*N*-hydrochloric acid at 24·3° ± 0·03.

Initial concentration of methyl acetate = 0·6857 mols. per litre.
" " " water = 51·74 " " "

t.	*x.*	*k.*	k_1.	k_2.
60	0·1192	0·00338	0·0000616	—
90	0·1747	0·00348	0·0000633	—
120	0·2183	0·00343	0·0000620	Mean
160	0·2746	0·00344	0·0000622	0·000284
280	0·4044	0·00349	0·0000628	—
340	0·4513	0·00351	0·0000629	—
460	0·5141	0·00343	0·0000613	—
∞	0·6482	—	—	—
	Mean.....	0·003465	0·0000623	0·000284

Table IV.

Hydrolysis of methyl acetate with 0·1*N*-hydrochloric acid at 25·00° ± 0·03.

Initial concentration of ester = 0·7013*N*.
" " " water = 52·19*N*.

t.	*x.*	*k.*	k_1.	k_2.
200	0·08455	0·000683	0·00001237	—
280	0·1171	0·000695	0·00001255	—
445	0·1727	0·000680	0·00001225	Mean
620	0·2311	0·000692	0·00001247	0·0000565
1515	0·4299	0·000691	0·00001235	—
1705	0·4588	0·000692	0·00001236	—
1930	0·4877	0·000698	0·00001254	—
∞	0·6624	—	—	—
	Mean.....	0·000690	0·00001236	0·0000565

Table V.

Catalyst: *N*-Hydrochloric acid at 25·0°.

Initial concentration in mols. of ester per litre.	No. of c.c. of ester in 50 c.c. of solution.	Mean concentration of water in mols. per litre = *w**.	*k.*	*k*/*w*.	k_1.	k_2.
1·741	8 approx.	45·38	0·00903	0·0001991	0·0001652	0·000755
1·151	5 "	48·76	0·00818	0·0001679	0·0001482	0·000677
0·7093	3 "	50·94	0·00764	0·0001467	0·0001392	0·000636

* The mean concentration of water is the concentration midway through an experiment, that is, when half the methyl acetate has been decomposed.

TABLE VI.

Catalyst: 0·5*N*-Hydrochloric acid at 24·3°.*

Initial concentration in mols. of ester per litre.	No. of c.c. of ester in 50 c.c. of solution.	Mean concentration of water in mols. per litre = w.†	k.	k/w.	k_1.	k_2.
1·744	8 approx.	46·10	0·00382	0·0000829	0·0000687	0·000313
1·155	5 ,,	49·14	0·00363	0·0000739	0·0000648	0·000295
0·6857	3 ,,	51·42	0·00346	0·0000674	0·0000623	0·000284
0·2420	1 ,,	53·73	0·00310	0·0000578	0·0000569	0·000256
0·1270	0·5 ,,	54·15	0·00300	0·0000553	0·0000551	0·000251

* The thermometer used in this series of measurements registered 25·0°, but on calibration was found to be in error.

† The mean concentration of water is the concentration midway through an experiment, that is, when half the methyl acetate has been decomposed.

TABLE VII.

Catalyst: 0·1*N*-Hydrochloric acid at 25·0°.

Initial concentration in mols. of ester per litre.	No. of c.c. of ester in 50 c.c. of solution.	Mean concentration of water in mols. per litre = w.	k.	k/w.	k_1.	k_2.
1·156	5 approx.	49·69	0·000726	0·00001461	0·00001302	0·0000595
0·7013	3 ,,	51·86	0·000690	0·00001330	0·00001236	0·0000565
0·2425	1 ,,	54·25	0·000660	0·00001217	0·00001177	0·0000538
0·1304	0·5 ,,	54·86	0·000606	0·00001104	0·00001093	0·0000499

Throughout each single experiment the values of k, k_1, and k_2 are constant within the experimental error, that is, there is no trend observable even in the most concentrated solutions of methyl acetate. From the summarising tables given above it will be seen that the values of the unimolecular constants k fall steadily with decreasing concentration of ester, as Ostwald has already shown; the values of k/w fall more rapidly still.

Also, the values of k_1—the true velocity-constant—still show the same decided fall, although not nearly so marked as that of k/w. The effect of the correction term k_2x^2 in the differential equation,

$$\frac{dx}{dt} = k_1(w - x)(b - x) - k_2x^2,$$

may be seen in the above tables by comparison of corresponding values of k/w and k_1. It is seen that these two values in the case of the most dilute solution of methyl acetate employed (0·1*N*) are identical within experimental error, but as the concentration of ester is increased k/w increases more rapidly than k_1.

Assuming the law of mass-action to be valid throughout, the constants given in the column headed k_1 should be of equal value,

as they include the correction for the reverse reaction, the formation of ester. Ostwald's statement, therefore, that the variation in the velocity-constants with change in the concentration of ester is due to there being an equilibrium point, is insufficient, and we must therefore consider other explanations to account for this variation. A first suggestion is that the concentration of the catalyst is not the same in each experiment; although the total concentration of hydrochloric acid is the same in each series, the degree of dissociation of the acid might change with the amount of ester present. Presumably the addition of the ester would decrease the dissociation of the acid, thus, lowering the hydrogen ion concentration; at first sight it appears, if this view be correct, that the velocity-constants should decrease as the concentration of the methyl acetate is increased.

However, from the recent work of Snethlage (*Zeitsch. physikal. Chem.*, 1913, **85**, 253), Acree (*Amer. Chem. J.*, 1912, **48**, 352) and others, the results of measurements of velocity of reaction can be interpreted so as to make it appear possible that the undissociated molecule of hydrochloric acid has a catalytic activity about twice as great as that of the hydrogen ion. On the assumption, then, that the presence of methyl acetate decreases the percentage ionisation of the catalysing acid, hydrochloric, it is to be expected that the velocity-constants should be greater the more ester is present. To test this, therefore, it is necessary to know the dissociation of the acid in each solution used, and for this purpose measurements of the conductivities of the acid in mixtures of water and methyl acetate were carried out.

Determination of the Degree of Dissociation of Hydrochloric Acid in Mixtures of Water and Methyl Acetate.

The electrical conductivities of several of the solutions used in the experiments on the velocity of the reaction were determined, and also those of solutions of $N/2000$-hydrochloric acid in the presence of varying amounts of methyl acetate. Assuming complete dissociation of the hydrochloric acid at the latter dilution, the degrees of dissociation for the other concentrations were calculated in the usual way. The ordinary Kohlrausch method and apparatus was used, the bridge being calibrated by Strouhal and Barus' method, whilst the cell constant was determined by the use of $N/50$-potassium chloride, which has a specific conductivity of 0·002728 at 24·3° and of 0·002768 at 25°. For the more dilute acid solutions the cell employed was of the Arrhenius type, whilst for the more concentrated solutions the conductivity vessel was a U-tube with closely fitting ebonite caps, which held the electrodes

firmly in position. Tables VIII. and IX. give the results of the measurements; interpolated values in these tables are bracketed.

The electrical conductivities of the solutions were determined immediately after making up and allowing them to attain the temperature of the thermostat, but no very great change was observed in the conductivities of the solution with time, the acetic acid gradually formed being very little dissociated in the presence of concentrated hydrochloric acid, whilst the hydrolysis of the ester is so slow with *N*/2000-hydrochloric acid that no difficulty presented itself. To obtain the specific conductivities of the more dilute acid solutions, that of the water ($1{\cdot}2 \times 10^{-6}$ mho) was subtrated from the observed conductivities. The small conductivity of the methyl acetate was, however, not subtracted, it being no doubt due chiefly to acetic acid, which even in the presence of *N*/2000-hydrochloric acid would be largely undissociated, and thus have very little influence on the final conductivity. No corrections for viscosity are introduced in the case of the results for *N*-hydrochloric acid, as the applicability of such a correction is doubtful in this case.

Table VIII.

Equivalent Conductivities and Degrees of Dissociation (α) *for* N- *and* N/10-*Hydrochloric Acid in Mixtures of Water and Methyl Acetate at* 25°.

Concentration of methyl acetate in mols. per litre.	Equivalent conductivity			α.	
	N-HCl.	*N*/10-HCl.	*N*/2000-HCl.	*N*-HCl.	*N*/10-HCl
1·741	247·4	—	336·8	0·734	—
1·151	274·8	—	370·2	0·742	(0·853)
0·704	296.8	344·5	396·9	0·748	0·868
0·2425	—	367·1	409·0	—	0·897
0·1300	—	374·4	412·5	—	0·908

Table IX.

Equivalent Conductivities and Degrees of Dissociation (α) *for* N/2-*Hydrochloric Acid in Mixtures of Water and Methyl Acetate at* 24·3°.

Concentration of methyl acetate in mols. per litre.	Equivalent conductivity		α.
	N/2-HCl.	*N*/2000-HCl.	for *N*/2-HCl.
1·744	262·6	333·0	0·789
1·155	—	—	(0·796)
0·6857	317·6	392·4	0·810
0·2420	—	—	(0·837)
0·1270	345·0	407·8	0·846

The above tables show that the degree of dissociation of HCl obtained in this way falls as the concentration of methyl acetate is increased.

Velocity-constants Corrected for the Change in the Degree of Dissociation of the Catalyst.

In order to correct the velocity-constants for the change in total catalyst, the most probable value of the ratio of the catalytic activity of the undissociated molecule of hydrochloric acid to that of the hydrogen ion must be ascertained. This "constant," which is denoted by k_M/k_H, is undoubtedly dependent on the reaction which is catalysed by the hydrochloric acid, and following Snethlage (*loc. cit.*) and H. S. Taylor (*Zeitsch. Elektrochem.*, 1914, **20**, 201) we take $k_M/k_H=2$, although this is probably only a first approximation. The correction is applied to the velocity-constants in the following way. If n be the concentration of the acid and α its degree of dissociation, then the catalytic power of the acid is given by the expression

$$n\alpha k_H + n(1-\alpha)k_M = n\alpha k_H + 2n(1-\alpha)k_H = nk_H(2-\alpha).$$

As k_H is a constant, its value is immaterial, and comparative corrected results are obtained by dividing the velocity-constants k_1, given in tables V., VI., and VII., by the corresponding values of $n(2-\alpha)$. This has been done, and the results are given in Tables X.—XII., the new velocity-constants being given in the column headed "Corrected velocity-constants."

TABLE X.

Velocity-constants with N-*Hydrochloric Acid at* 25° *Corrected for the Change in Catalytic Activity of the Acid.*

Concentration of methyl acetate.	α for N-HCl.	k_1.	Corrected velocity-constants.
1·741N	0·734	0·0001652	0·0001305
1·151N	0·742	0·0001482	0·0001179
0·7093N	0·748	0·0001392	0·0001112

TABLE XI.

Velocity-constants with 0·5N-*Hydrochloric Acid at* 24·3° *Corrected for the Change in Catalytic Activity of the Acid.*

Concentration of methyl acetate.	α for 0·5 N-HCl.	k_1.	Corrected velocity-constants.
1·744N	0·789	0·0000686	0·0001134
1·155N	0·796	0·0000648	0·0001076
0·6857N	0·810	0·0000623	0·0001047
0·2420N	0·837	0·0000569	0·0000978
0·1270N	0·846	0·0000551	0·0000955

TABLE XII.

Velocity-constants with 0·1N-*Hydrochloric Acid at* 25·0° *Corrected for the Change in Catalytic Activity of the Acid.*

Concentration of methyl acetate.	α for 0·1 *N*-HCl.	k_1.	Corrected velocity-constants.
1·156*N*	0·853	0·00001302	0·0001135
0·7013*N*	0·768	0·00001236	0·0001091
0·2425*N*	0·897	0·00001177	0·0001067
0·1304*N*	0·908	0·00001093	0·0001001

The values in the column headed "Corrected velocity-constants" in the three above tables exhibit the same rise on increasing the concentration of the ester, although not so markedly as the k_1 values themselves; that is, the introduction of the correction which allows for the actual change in the degree of dissociation of the acid as the concentration of ester increases, and also allows for the catalytic activity of the undissociated molecule of hydrochloric acid, is insufficient to explain the phenomenon quantitatively. This assumes that the conductivity method gives correct values for α and that the value of k_M/k_H is 2. It is important to notice that in order to make all the corrected constants of table XI. identical it would be necessary to assume k_M/k_H to be of the order 20—a value which on other grounds is inadmissible. The abnormality still remains.

In order, however, to make certain that the phenomenon is not connected with the fact that in the case of hydrochloric acid the value of k_M is greater than that of k_H (that is, the undissociated molecule more catalytically active than the hydrogen ion), it was thought advisable to repeat the experiments, using as catalyst another acid, for which k_M/k_H is known to be less than unity. Trichloroacetic acid was eventually chosen, it having the advantage of being a very strong acid with a dissociation-constant of 1·21 at 25°, and H. S. Taylor (*Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 37) has shown conclusively that the catalytic activity of its undissociated molecule is about a third that of the hydrogen ion.

Experiments using Trichloroacetic Acid as Catalyst.

The trichloroacetic acid first obtained melted fairly sharply at 55° (corr.), and in order to purify it from any possible liquid impurities it was allowed to drain for two days on a porous plate in a vacuum. The resulting acid melted at 56°, but a suitable solvent from which to recrystallise it was not found. That there was no serious amount of impurity present was shown by a deter-

mination of its equivalent. Two experiments on the velocity of hydrolysis of methyl acetate were carried out at 25°, using 0·5*N*-trichloroacetic acid as catalyst, the concentration of the ester being 1 and 5 c.c. respectively in 50 c.c. of solution. The former gave a unimolecular constant of 0·00250, whilst the latter gave a constant which rose slightly from 0·00260 to 0·00279. With regard to the latter experiment, a distinct odour of the methyl ester of trichloroacetic acid was observed after the reaction was completed, and the formation of this ester is presumably the cause of the rising "constant." In any case, the second constant for the hydrolysis of 5 c.c. of ester is unmistakably higher than the former, the hydrolysis of 1 c.c. of ester, so that the same effect is observed as in the presence of hydrochloric acid as the catalyst. However, the presence of trichloroacetic acid complicates the system, as the acid combines with some methyl alcohol, and therefore no attempt could be made to determine the equilibrium-constant of the reaction

$$CH_3{\cdot}CO_2{\cdot}CH_3 + H_2O \rightleftharpoons CH_3{\cdot}OH + CH_3{\cdot}CO_2H$$

in the presence of trichloroacetic acid, and thus to calculate the true velocity-constant of the hydrolysis, k_1. From analogy, however, to the case in which hydrochloric acid is the catalyst, if the unimolecular constants are increased as the ester content increases, so also are k_1 and k_2. An experiment was also attempted with 0·5*N*-trichloroacetic acid as catalyst and 8 c.c. of methyl acetate in 50 c.c. of solution, but in this case two liquid layers resulted, the heavier being chiefly trichloroacetic acid and methyl acetate. The above two experiments, however, are sufficient to show that the same effect is observed using trichloroacetic acid as catalyst as with hydrochloric acid, that is, the velocity of hydrolysis increases as the initial concentration of the ester is increased. It was shown for the case of hydrochloric acid that, correcting for the reverse reaction, the formation of ester did not account for the change, and it is very probable that the same is the case with trichloroacetic acid as the catalyst. The increase in the value of the velocity-constant with increase in initial concentration of the ester is therefore not causally connected with a particular catalysing acid.

Experiments with More Concentrated Solutions of Methyl Acetate.

All the experiments described up to this point gave well-agreeing velocity-constants, but it was found that further increase in the concentration of the ester caused a rising velocity "constant" throughout a single determination. The figures given in table XIII. illustrate this. The concentration of the ester was about

13 c.c. in 50 c.c. of solution, that of the catalyst (hydrochloric acid) 0·5*N*, and the temperature 24·3°.

TABLE XIII.

Time from start.	Unimolecular constant, *k*.	Time from start.	Unimolecular constant, *k*.
39·0 minutes	0·003926	240·3 minutes	0·004176
74·5 ,,	0·003900	281·3 ,,	0·004249
120·3 ,,	0·003914	333·6 ,,	0·004273
200·3 ,,	0·004146	402·1 ,,	0·004491

The unimolecular constant *k* steadily rises. With a concentration of ester of 10 c.c. in 50 c.c. of solution there was also a rise, which although definite was not so pronounced as in the case of 13 c.c. In the former case the "constant" rose from 0·00387 at the commencement of the reaction to 0·00414 at the end, whilst with 8 c.c. of ester, on the other hand, no deviation from constancy in *k* could be observed. This particular phenomenon was not pursued further, and is only introduced here because of its bearing on the results given above concerning the rise in the velocity-constants when the initial concentration of ester is increased.

Discussion of Results.

The problem raised by the results obtained in the present work is the mode of expressing the active mass of a constituent which acts stoicheiometrically and also catalytically (as solvent). In the first place, it may be pointed out that the substitution of osmotic pressure for concentration as a more correct measure of active mass, a suggestion made by Arrhenius (*Zeitsch. physikal. Chem.*, 1899, **28**, 317) in the analogous case of inversion of sucrose, does not correspond to the facts, a conclusion already reached by Rosanoff (*loc. cit.*). In the second place, it may be suggested that the dependence of the velocity-constant on the initial conditions is due to the formation of intermediate compounds, which function as the reactants and resultants respectively. The simplest assumption to make is that the ester and water first produce an additive compound, which is catalytically decomposed into methyl alcohol and acetic acid.

Applying the principle of mass action to the instantaneous formation of complex, namely,

$$\text{ester} + \text{water} \rightleftarrows (\text{ester, water}),$$

it is evident that a greater quantity of complex will be formed on increasing the ester concentration at the expense of the water up to a certain composition of the mixture. This suggestion may be applied in the following way. If the concentration of ester be

initially a gram-molecules per litre, that of the water w, and that of the complex e gram-molecules, the equilibrium will be given by the relation

$$K'(a-e)(w-e)=e,$$

where K' is the equilibrium-constant. Since in the experiments already described a is small compared with w, e must be still smaller, so that we can rewrite the above relation thus:

$$K'(a-e)w=e \text{ or } e=\frac{K'wa}{1+K'w},$$

If the complex be the reactive substance we have at the beginning (when the reverse reaction is negligible) for the velocity of reaction

$$\frac{dx}{dt}=k_{\text{true}} \times e = k_{\text{true}} \times \frac{K'wa}{1+K'w}.$$

where k_{true} stands for the velocity-constant of decomposition of the complex. On the other hand, the equation usually employed takes the form

$$\frac{dx}{dt}=k_{\text{obs.}} \times a \times w.$$

where k_{obs} is the velocity-constant actually measured.

It follows, therefore, that

$$k_{\text{obs.}}=k_{\text{true}} \times \frac{K}{1+K'w}.$$

This relation may be tested by calculating by its aid values of the equilibrium-constant K' by taking any two values of $k_{\text{obs.}}$ corresponding with two values of w. This has been done, employing the series of "corrected velocity-constants" given in table XI. Six negative and four positive values of K' were obtained. The equation was also applied to the analogous case of the inversion of sucrose, the data being those of Ostwald, Spohr, and Rosanoff (compare Rosanoff, *loc. cit.*). In all cases a negative value for K' is the result. The negative value has, of course, no physical significance, but its frequency of occurrence suggests that it is not due to experimental error.

It will be seen, however, on inspection of the data that the cause of the negative sign is the fact that the (observed) velocity-constant rises too rapidly for a given diminution in initial water-content, that is, the values of e are greater (as the water-content diminishes) than would be anticipated on the basis of mass-action alone. If we accept the explanation that the reactive substance is the additive compound, then it follows that the solvent is exerting a catalytic effect at the same time in the sense that diminution in the water favours the production of the complex. This

is in agreement with what one would expect in view of the strongly dissociating power of water. As the initial water-content is diminished, the medium becomes richer in methyl acetate, and therefore as a whole must act as a feebler dissociating agent on the additive complex (ester, water), which is therefore produced in greater quantity than would be the case if the physical action of the solvent remained constant. This explains not only the apparent negative catalytic effect of water in this case, but likewise its negative catalytic effect on the rate of esterification investigated by Lapworth and Fitzgerald (T., 1908, **93**, 2174), although in the latter case the water plays no "stoicheiometric" part.

In view of the evidence obtained from spectroscopic measurements in the infra-red region, described in Part III. of this series, in favour of the existence of an ester–water complex, the suggestion of a simultaneous stoicheiometric and anticatalytic rôle on the part of the water present as an explanation of the variation of velocity-constant with initial composition of the system receives considerable support. The conclusion is also reached that the phenomenon must be a general one, since solvation appears to be general and all liquids possess dissociating power to some degree. This also is borne out by a number of cases quoted by van't Hoff ("Studies in Chemical Dynamics," p. 28), who concludes that "it may therefore also happen that one of the liquid bodies which is taking part in the reaction is itself an unfavourable medium." Negative catalysis by one of the constituents of the solvent is therefore not exceptional, even when the constituent participates stoicheiometrically at the same time. Naturally, dissociating power itself requires a physical mechanism. It is suggestive that Kruger (*Zeitsch. Elektrochem.*, 1911, **17**, 453) attributes it to the presence of infra-red radiation.

Summary.

(1) Measurements of the velocity of hydrolysis of methyl acetate with varying initial concentrations of the ester have been carried out, using as catalysts 0·1*N*-, 0·5*N*-, and *N*-hydrochloric acid, and also 0·5*N*-trichloroacetic acid. It is found that the unimolecular constants k and the constants k_1, which are corrected for the reverse reaction, were constant in each experiment, but their value depended on the initial composition of the system, the value rising with the concentration of the ester.

(2) This increase is not accounted for by correcting the constants for the change in catalysing power of the acid due to the change in the degree of dissociation as more ester is added.

(3) The equilibrium-constant of the reaction between water and methyl acetate has been redetermined, and is found to be 4·6 in the presence of hydrochloric acid not exceeding *N* in strength.

(4) The variation in velocity-constant with initial conditions can be explained if the reacting substance is considered to be an ester–water additive complex the degree of dissociation of which decreases as the water-content decreases, that is, the water acts stoicheiometrically and at the same time as a negative catalyst in virtue of its high dissociating power.

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VII.—"*The Propagation of Flame in Mixtures of Hydrogen and Air. The 'Uniform Movement.'*"

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THE work described in this paper was carried out at the Home Office Experimental Station under the direction of Dr. R. V. Wheeler, and is a revision of Mallard and Le Chatelier's work on the same subject (*Ann. des Mines*, 1883, [viii], **4**, 314). Such a revision seemed necessary in the light of Wheeler's recent work on the propagation of flame in mixtures of methane and air (T., 1914, **105**, 2606), which shows considerable divergence from Mallard and Le Chatelier's results (*loc. cit.*, p. 324).

Mixtures of hydrogen and air differ in their behaviour from mixtures of methane and air when ignited in horizontal tubes, inasmuch as in the former case the flame travels more rapidly, and in some mixtures of hydrogen and air the explosion wave may be developed after the flame has travelled a short distance (about 2 metres) from the open end of the tube. The phenomena that precede the development of the explosion wave, or which occur when the explosion wave is not set up, are, however, similar to those that obtain with all mixtures of methane and air. Thus, when the mixture is ignited at the open end of a horizontal tube, which is closed at the other end, a "uniform movement" of the flame is set up, which is succeeded by a "vibratory movement." The present paper deals solely with the uniform movement.

The uniform movement of flame, defined by Le Chatelier ("Leçons sur le Carbone," Paris, 1908, p. 273), as resulting from the normal transference of heat from layer to layer of the mixture

by radiation and conduction, is, according to Wheeler (see Bone's Presidential Address to Section B, British Association, 1915), a limited phenomenon, obtainable only in tubes within a certain range of diameter, large enough to prevent appreciable cooling by the walls, but narrow enough to suppress the influence of convection currents.

The diameter of the tube, requisite to ensure that cooling by the walls shall not affect the speed of flame, is, according to Mallard and Le Chatelier, "d'autant plus grand que la vitesse de propagation de la flamme est plus faible" (*loc. cit.*, p. 320). According to the following series of experiments made by them with a mixture of hydrogen and air containing 30 per cent. of the combustible gas, in which the speed of propagation of flame is fairly rapid, a diameter of 3 mm. should suffice for this purpose.

Diameter of tube.	Speed of uniform movement.
10 mm.	350 cm. per sec.
6 ,,	325 ,, ,,
3 ,,	350 ,, ,,

We have made three series of experiments with a number of mixtures of hydrogen and air, ranging from the lower to the upper limit of inflammability, using tubes of 9, 11·5, and 25 mm. in diameter respectively. We are unable to confirm the said conclusion that the speed of the flame in a given mixture is independent of the diameter of the tube above 3 mm. On the contrary, over a great part of the range of inflammability of such mixtures the speeds are some 25 to 30 cm. per second faster in tubes 11·5 mm. than in tubes 9 mm. in diameter; whilst in tubes 25 mm. in diameter the speeds are between 75 and 100 cm. per second faster than in a tube of 9 mm. diameter over two-thirds of the range of inflammability.

In their series of determinations of the speed of flame in different mixtures of hydrogen and air, Mallard and Le Chatelier used a tube 10 mm. in diameter, the length of which was varied, and they measured the velocity over the first metre. They thereby included in most of their measurements (as they themselves subsequently realised) part of the "vibratory movement," since the uniform movement does not, in the majority of mixtures of hydrogen and air, extend over so great a distance as 1 metre. Their general conclusions regarding the variation in the speed of flame with the hydrogen content of the mixture were as follows:

(1) The maximum speed is not obtained with the mixture containing hydrogen and oxygen in combining proportions (29·5 per cent. of hydrogen), but with a mixture containing 40 per cent. of hydrogen.

(2) On either side of the maximum the speeds vary proportionately with the hydrogen contents of the mixtures.

We can in part confirm the first of these statements. The maximum speed of propagation of flame, according to our determinations, is obtained with mixtures over the range 38—45 per cent. of hydrogen. The explanation advanced by Le Chatelier ("Leçons sur le Carbone," p. 279) is that the rate of transmission of heat from the burnt to the unburnt layer of mixture (and, *pro tanto*, the rate of propagation of flame) depends, not only on the temperature of combustion of the mixture, but on its thermal conductivity. The thermal conductivity of hydrogen is six times that of air, and it may well be that with mixtures containing more than one-third of their volume of hydrogen the enhanced conductivity of the mixture more than compensates for its lower heating value. In the case of mixtures of methane and air, the range of inflammability of which lies between 5·4 and 14·3 per cent. of methane, Wheeler (*loc. cit.*, p. 2608) has shown that no such effect is noticeable. The thermal conductivity of methane is $6{\cdot}47 \times 10^{-5}$, compared with air, $5{\cdot}22 \times 10^{-5}$, and with hydrogen, $31{\cdot}9 \times 10^{-5}$.

Our experiments do not, however, bear out Mallard and Le Chatelier's second statement. As already stated, the maximum speed is obtained with mixtures containing between 38 and 45 per cent. of hydrogen, and not with one particular mixture.

Le Chatelier, in further comment on this subject ("Le Carbone," p. 279), states that "la courbe, représentant les vitesses en fonction de la proportion de gaz combustible, est composée de deux droites, se coupant à angles vifs pour la proportion de 40 p. 100 hydrogène, avec une vitesse maximum de 4 met. 37 cm. par seconde." However, in the figure (Fig. 36, p. 278) illustrating this statement he adopts 485 instead of 437 cm. per sec. as the velocity for a mixture containing 40 per cent. of hydrogen.*

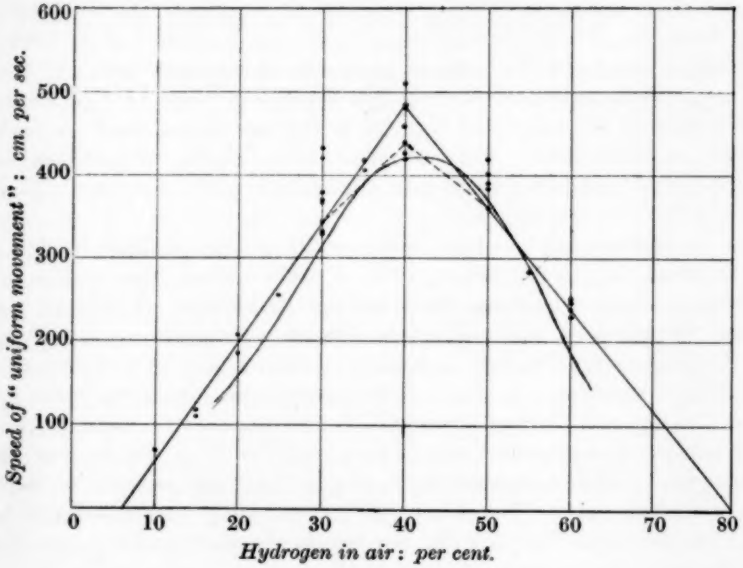
In Fig. 1 are plotted all the determinations recorded by Mallard and Le Chatelier, and the curve (two straight lines) deduced by them therefrom; as well as, for purposes of comparison, a curve derived from one series of our experiments with a tube 9 mm. in diameter. In dotted line is shown the upper portion of their curve as it appears when the figure given in the text and in the table of experiments (437 cm. per sec.) is taken for the velocity of the mixture containing 40 per cent. of hydrogen. The entire

* It may be noted that the same figure, 437 cm. per sec. is given by Mallard and Le Chatelier in the account of their researches in the *Ann. des Mines*, (*loc. cit.*), whereas here also the curve is drawn taking 485 cm. per sec. as the maximum speed.

curve now conforms more nearly with that indicated by our own experiments. It will be seen that the central portion of our curve is parabolic, whilst the extremities show a tendency to become horizontal.

Although the latter tendency is not so marked as with mixtures of methane and air, it is sufficient to render unjustifiable Mallard and Le Chatelier's prolongation of either limb of the curve to the zero velocity ordinate to determine the limits of inflammability, and accordingly their figures of 6 per cent. and 80 per cent. of hydrogen in air as the lower and upper limits of inflammability

FIG. 1.



respectively, must be regarded as erroneous. We have made no attempt to determine accurately the limits for horizontal propagation of flame in mixtures of hydrogen and air, but are satisfied that in a tube 9 mm. in diameter flame does not travel in mixtures at normal temperature and pressure containing 11·8 per cent. or less, or 63·5 per cent. or more of hydrogen.

An examination of the curves derived from our experiments, shown in Fig. 2, indicates that whereas an increase in the diameter of the tube in which the flame is travelling enhances the speed for many mixtures, mixtures rich in hydrogen are not appreciably affected. Thus, with mixtures containing up to 35 per cent. of hydrogen, the speeds in an 11·5 mm. tube are faster than in a

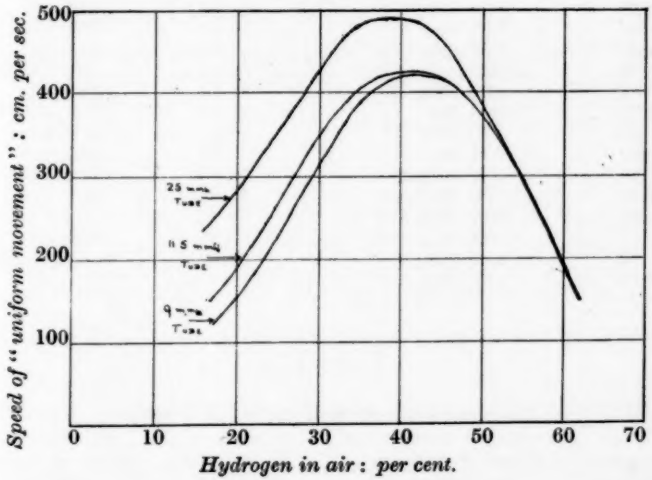
9 mm. tube; whilst with a 25 mm. tube the speeds in mixtures containing up to 54 per cent. of hydrogen are considerably faster than those obtained in either a 9 mm. tube or in an 11·5 mm. tube; but the speeds in the richer mixtures are almost identical in the three tubes. These results seem to indicate that the influence of cooling by the walls of the tubes on the speeds of the flames becomes nearly negligible when the thermal conductivity of the gaseous mixture is high.

Experimental.

The method of experiment and the electrical means of recording the speeds were similar to those employed by Wheeler for mixtures of methane and air (*loc. cit.*, p. 2609).

Glass tubes of three different diameters were used for separate

Fig. 2.



series of experiments, each about 1·5 metres long, closed at one end by a tap, and connected at the other to a gas-holder by rubber tubing, which could readily be removed when it was desired to ignite the mixture, leaving the end open.

The speeds were determined between two points 40 cm. apart, the first point being 10 cm. from the point of ignition, which was the open end of the tube. Ignition was effected by a lighted taper held to the open end as soon as the rubber tubing connecting with the gas-holder had been removed.

The hydrogen used was obtained (from the British Oxygen Company) compressed in cylinders, and was of 99·5 per cent. purity. The mixtures were made in iron gas-holders of 70 litres capacity,

over water rendered slightly alkaline by potassium hydroxide. The mixture to be experimented with, which was analysed before use, was allowed to flow slowly through the explosion tube to displace air, six times the volume of the tube being used. The initial temperature of the mixture was that of the room (15—20°), and it was saturated with water-vapour at that temperature.

All the determinations of speeds made are given in the tables that follow.

TABLE I.

Internal diameter of tube, 9 mm.

Hydrogen in mixture. Per cent.	Speed of uniform movement. Cm. per sec.	Hydrogen in mixture. Per cent.	Speed of uniform movement. Cm. per sec.
11·80	No propagation.	43·10	413, 420, 433
17·30	124, 126	46·80	393, 394, 412
21·60	166, 175, 176	48·80	379, 387
21·95	173, 194	50·40	352, 365, 369
23·65	197, 203, 206	50·55	353, 354
24·70	231	51·15	354, 356
25·15	221, 223, 237	51·55	346, 353
27·25	260, 264	55·25	299, 328, 333
27·80	273, 278	57·00	275, 282
30·45	312, 321, 321	57·15	259, 277
33·85	370, 373, 391	58·95	223, 224
33·90	360, 368, 400	59·05	208, 216
36·55	388, 394, 394	59·45	172
37·15	384, 412, 412	62·00	150, 157, 162
40·10	415, 424, 424	63·50	No propagation.
42·70	394, 395, 416		

TABLE II.

Internal diameter of tube, 11·5 mm.

Hydrogen in mixture. Per cent.	Speed of uniform movement. Cm. per sec.	Hydrogen in mixture. Per cent.	Speed of uniform movement. Cm. per sec.
17·30	148, 154	46·80	398, 419
22·70	212, 218	48·80	370, 410
25·15	245, 265, 267	51·15	348, 350
27·25	280, 287, 299	51·55	341, 352, 382
27·80	294	55·25	303, 309, 319
33·90	383	57·15	261, 280
37·15	390, 415	58·95	175, 180
40·10	400, 421	59·45	173, 177
43·10	411, 435		

TABLE III.

Internal diameter of tube, 25 mm.

Hydrogen in mixture. Per cent.	Speed of uniform movement. Cm. per sec.	Hydrogen in mixture. Per cent.	Speed of uniform movement. Cm. per sec.
20·15	255, 259, 279	47·00	430, 430
26·10	354, 354	47·70	411, 433, 433
29·70	403, 408, 408	49·15	380, 383, 398
31·50	435, 437, 453	54·80	309, 317, 320
36·30	480, 480, 503	60·25	153, 162, 162
40·50	463, 483, 500	61·60	139, 149, 150
44·55	437, 460, 478		

We wish to express our thanks to Mr. T. Mason, of the Home Office Experimental Station, who prepared and analysed the gas mixtures, and also to Dr. R. V. Wheeler and Professor W. A. Bone for helpful criticism of our results.

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VIII.—*Polymorphism in Halogen-substituted Anilides.*

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ALTHOUGH ability to crystallise in more than one form appears to be a general property of the anilides, few of the modifications, unstable in ordinary circumstances, have been described. They are formed only under favourable conditions as a first stage in the process of crystallisation, and then more or less rapidly redissolve and disappear; their transformation, therefore, unless accompanied by some colour change, may easily pass unobserved.

Descriptions of the phenomena attending the crystallisation of aceto-*p*-bromo- and aceto-2:4-dibromo-anilide (Chattaway and Lambert, T., 1915, **107**, 1766) and propiono-*p*-iodoanilide (Chattaway and Constable, T., 1914, **105**, 126) have recently been published; the present paper gives an account of the similar behaviour of other derivatives of 2:4-dihalogen-substituted anilines.

Both aceto-2-chloro-4-bromo- and 4-chloro-2-bromo-anilide can exist in two modifications. When a saturated solution of either in glacial acetic acid is allowed to cool undisturbed, an unstable, needle-shaped modification at first separates, the long, interlaced crystals com-

pletely filling the liquid. In the crystalline mass compact crystals of a stable form soon make their appearance; the needle-shaped crystals dissolve, and the compact crystals grow until the conversion is complete. If only a few crystals of the stable form appear, they grow slowly if the crystalline mass of the unstable form is left undisturbed; but if it is stirred the transformation is complete in a few seconds, small crystals of the compact form falling as a crystalline precipitate.

The transformation of the unstable into the stable form of aceto-2-chloro-4-bromoanilide is much more rapid than the corresponding transformation of aceto-4-chloro-2-bromoanilide.

The *p*-nitrobenzoyl derivatives of the 2:4-dihalogen-substituted anilines also all crystallise in two forms. On cooling hot saturated alcoholic solutions they separate in slender needles, or hairs, which convert the liquid into a felt-like mass. After a time crystals of the stable compact forms make their appearance, the original crystals disappear, and the new crystals grow until conversion is complete. Of the *p*-nitrobenzanilides, *p*-nitrobenzo-2-chloro-4-bromoanilide changes most rapidly; if the liquid containing the hair-like form in suspension is shaken, conversion is complete in a few minutes. In a series of comparative experiments in which similar amounts of solution were used and the felted masses of hair-like crystals were allowed to transform undisturbed, about three days were required in the cases of *p*-nitrobenzo-4-chloro-2-bromoanilide and of *p*-nitrobenzo-2:4-dibromoanilide, whilst in the case of *p*-nitrobenzo-2:4-dichloroanilide several weeks elapsed before all the unstable form had disappeared.

Experimental.

Preparation of 2:4-*Dibromoaniline.*

The preparation of 2:4-dibromoaniline has always offered considerable difficulty. The action of bromine on aniline dissolved in glacial acetic acid is so energetic that in practice it cannot be checked at intermediate stages, the substituted product, even if a small quantity of bromine is used, being mainly 2:4:6-tribromoaniline, or if excess of bromine is used, the stable perbromide of this compound, $C_6H_2Br_3 \cdot NH_2,HBr_3$. The action of bromine on acetanilide is less vigorous, and if a gram-molecule of bromine is added to a gram-molecule of acetanilide dissolved in acetic acid in the presence of a gram-molecule of sodium acetate, aceto-*p*-bromoanilide is quantitatively and exclusively produced. A second atom of bromine can only be made to enter the acetanilide with much greater difficulty, some hours of action at a high temperature being

required. During the necessary heating, if any water is present hydrolysis takes place so easily, even in the presence of excess of sodium acetate, that further action results in the production of 2:4:6-tribromoaniline, just as if aniline itself had been employed.

This, however, can be avoided, and aceto-2:4-dibromoanilide can be quantitatively obtained if precautions are taken to avoid the presence of hydrobromic acid and of water. The best procedure is as follows: A gram-molecule of aceto-*p*-bromoanilide * and a gram-molecule of fused and finely powdered sodium acetate are suspended in sufficient glacial acetic acid to make a thick paste. A gram-molecule of bromine dissolved in eight to ten times its volume of glacial acetic acid is added slowly, and the mixture heated for five to six hours on a water-bath until the colour of bromine has almost disappeared. On diluting the cooled product with water, aceto-2:4-dibromoanilide (m. p. 146°) separates, and should be immediately filtered off and crystallised from alcohol. The aniline is obtained by dissolving the anilide in boiling alcohol mixed with about one-eighth of its bulk of concentrated hydrochloric acid, boiling the liquid under a reflux condenser for eight to nine hours, distilling off the alcohol in a current of steam, and adding a slight excess of sodium hydroxide to the cooled residue. The aniline separates as a white, crystalline mass (m. p. 78—79°), the yield being about 90 per cent. of the quantity theoretically obtainable from the aceto-*p*-bromoanilide used. The aniline may be obtained free from colour by distillation in a current of steam, but this is somewhat tedious if large quantities are required, and it is quite unnecessary if the base is to be used for subsequent preparations.

Preparation of 2-Chloro-4-bromoaniline and 4-Chloro-2-bromoaniline.

The preparation of 2-chloro-4-bromoaniline offers no difficulty, as the corresponding aceto-2-chloro-4-bromoanilide is easily prepared either by the action of chlorine on aceto-*p*-bromoanilide or of bromine on aceto-*o*-chloroanilide. The former method is more convenient, as *p*-bromacetanilide is so easily procured. The process is best carried out by passing the requisite amount of chlorine into a cooled suspension in glacial acetic acid of one gram-molecule of aceto-*p*-bromoanilide and one gram-molecule of anhydrous sodium acetate. The action proceeds easily at the ordinary temperature, and after precipitation by dilution and crystallisation from alcohol, aceto-2-chloro-4-bromoanilide (m. p. 151°) is obtained in good yield. This

* Acetanilide may be used employing double the quantity of sodium acetate and of bromine.

can then easily be converted into 2-chloro-4-bromoaniline (m. p. 73°) by the method previously described.

In order to effect the entrance of a bromine atom into the ortho-position in aceto-*p*-chloroanilide, several hours' heating on a water-bath are required. The method which has been found most convenient is similar to that described for the preparation of aceto-2:4-dibromoanilide. The presence of hydrobromic acid and of water must be similarly avoided. An excellent yield of pure aceto-4-chloro-2-bromoanilide (m. p. 137°) is obtained in this way from aceto-*p*-chloroanilide, and from this 4-chloro-2-bromoaniline (m. p. 69°) can be obtained, as above described.

Polymorphic Forms of the Acetochlorobromoanilides.

When a nearly saturated solution of aceto-2-chloro-4-bromoanilide in boiling glacial acetic acid is allowed to cool slowly, no separation of crystals takes place as a rule until the liquid has reached a temperature not far removed from the ordinary; tufts of fine, needle-shaped crystals of an unstable modification then appear, often floating in the liquids, and grow steadily; very soon compact crystals of the stable form make their appearance, generally on the surface of the liquid, and having reached a moderate size fall in a shower to the bottom, the tufts of the needle-shaped modification dissolving and disappearing. The transformation is usually so rapid that unless the cooling liquid is observed with a lens the tufts of the unstable crystals may easily escape notice.

When a small quantity of such a hot saturated solution in glacial acetic acid is cooled rapidly in ice the unstable modification separates at a few points in small tufts of very slender prisms, which grow rapidly until a felted mass of interlaced, fine crystals is formed. These, if left undisturbed, may remain for several days before crystalline nuclei of the stable, compact, rhombic form make their appearance and grow slowly, but if a few crystals of the stable form are added and the mass is stirred, transformation takes place very rapidly, and in a few seconds the needle-shaped modification dissolves and disappears, and is replaced by small crystals of the compact form, which sink to the bottom of the liquid as a crystalline precipitate. An alcoholic solution of aceto-2-chloro-4-bromoanilide behaves similarly when cooled.

Aceto-4-chloro-2-bromoanilide also crystallises in two polymorphic forms. Transformation of the unstable into the stable form is not so rapid as in the case of the isomeric compound.

When a nearly saturated solution in hot glacial acetic acid is boiled for some time to destroy all crystalline nuclei and then allowed to cool slowly, the unstable modification separates in clusters

of slender needles, which completely fill the liquid; these, if left undisturbed, may remain without change for days, but sooner or later crystals of the compact, stable modification make their appearance, and grow slowly to a considerable size, the unstable form dissolving and disappearing after some hours.

If a few crystals of the stable modification are introduced into the felted mass of needle-shaped crystals and the whole is vigorously stirred, transformation is complete in a few minutes, small crystals of the compact form being the product.

A number of derivatives of the 2:4-dihalogen-substituted anilines, not hitherto described, have been prepared in order to ascertain which can easily be obtained in two forms. The butyranilides were prepared by heating butyric anhydride with equivalent amounts of the various anilines.

n-*Butyro*-2-*chloro*-4-*bromoanilide*,

$$C_6H_3ClBr\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CH_3,$$

is very readily soluble in alcohol, but less readily so in light petroleum. It crystallises in long, colourless needles melting at 110°; extinction, 21°:

0·2234 gave 0·2682 AgCl + AgBr. Cl = 12·85; Br = 28·97.
$C_{10}H_{11}ONClBr$ requires Cl = 12·82; Br = 28·90 per cent.

n-*Butyro*-4-*chloro*-2-*bromoanilide* is very readily soluble in alcohol, but less readily so in a mixture of light petroleum and benzene. It crystallises in colourless needles melting at 111·5°; extinction, 31°:

0·2275 gave 0·2730 AgCl + AgBr. Cl = 12·84; Br = 28·96.
$C_{10}H_{11}ONClBr$ requires Cl = 12·82; Br = 28·90 per cent.

The phenylacetanilides were prepared by the interaction of equivalent quantities of phenylacetyl chloride, and the aniline dissolved in ether, in the presence of an equivalent weight of pyridine.

Phenylaceto-2-*chloro*-4-*bromoanilide*,

$$C_6H_3ClBr\cdot NH\cdot CO\cdot CH_2\cdot C_6H_5,$$

crystallises from boiling alcohol, in which it is readily soluble, in colourless needles melting at 150°; extinction variable:

0·2187 gave 0·2233 AgCl + AgBr. Cl = 10·93; Br = 24·64.
$C_{14}H_{11}ONClBr$ requires Cl = 10·92; Br = 24·63 per cent.

Phenylaceto-4-*chloro*-2-*bromoanilide* crystallises from boiling alcohol, in which it is readily soluble, in long, colourless needles melting at 148°:

0·1536 gave 0·1568 AgCl + AgBr. Cl = 10·92; Br = 24·64.
$C_{14}H_{11}ONClBr$ requires Cl = 10·92; Br = 24·63 per cent.

Phenylaceto-2 : 4-*dibromoanilide*, $C_6H_3Br_2\cdot NH\cdot CO\cdot CH_2\cdot C_6H_5$, crystallises from alcohol in long, colourless needles melting at 160°:

0·1520 gave 0·1548 AgBr. Br = 43·34.

$C_{14}H_{11}ONBr_2$ requires Br = 43·32 per cent.

The nitrobenzo-2:4-dihalogen-substituted anilides were prepared by adding the nitrobenzoyl chlorides to equivalent amounts of the anilines dissolved in ether in the presence of pyridine or of a concentrated solution of sodium carbonate.

o-*Nitrobenzo-2-chloro-4-bromoanilide*,

$$C_6H_3ClBr\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

is fairly readily soluble in boiling alcohol, from which it crystallises in colourless needles melting at 165°; extinction, 25°:

0·1788 gave 0·1663 AgCl + AgBr. Cl = 9·96; Br = 22·44.

$C_{13}H_8O_3N_2ClBr$ requires Cl = 9·97; Br = 22·48 per cent.

o-*Nitrobenzo-2:4-dibromoanilide*,

$$C_6H_3Br_2\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

is readily soluble in boiling glacial acetic acid, but less readily so in boiling alcohol, than the compound just described. It crystallises from alcohol in pale yellow, slightly oblique plates melting at 178°; extinction, 24°:

0·2060 gave 0·1937 AgBr. Br = 40·01.

$C_{13}H_8O_3N_2Br_2$ requires Br = 39·96 per cent.

o-*Nitrobenzo-4-chloro-2-bromoanilide* is fairly readily soluble in boiling alcohol, and crystallises in colourless, slightly oblique plates melting at 166°; extinction, 18°:

0·2153 gave 0·2005 AgCl + AgBr. Cl = 9·97; Br = 22·47.

$C_{13}H_8O_3N_2ClBr$ requires Cl = 9·97; Br = 22·48 per cent.

o-*Nitrobenzo-2:4-dichloroanilide*,

$$C_6H_3Cl_2\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

is readily soluble in boiling alcohol, from which it crystallises in colourless, oblique plates melting at 153·5°:

0·2299 gave 0·2116 AgCl. Cl = 22·77.

$C_{13}H_8O_3N_2Cl_2$ requires Cl = 22·80 per cent.

m-*Nitrobenzo-2-chloro-4-bromoanilide* is sparingly soluble in boiling alcohol, but readily so in boiling glacial acetic acid, from which it crystallises in long, colourless needles melting at 191°:

0·1971 gave 0·1830 AgCl + AgBr. Cl = 9·94; Br = 22·41.

$C_{13}H_8O_3N_2ClBr$ requires Cl = 9·97; Br = 22·48 per cent.

m-*Nitrobenzo-2:4-dibromoanilide* is moderately readily soluble in both alcohol and glacial acetic acid, and crystallises in colourless needles melting at 165°; extinction variable:

0·1990 gave 0·1860 AgBr. Br = 39·77.

$C_{13}H_8O_3N_2Br_2$ requires Br = 39·96 per cent.

m-*Nitrobenzo-4-chloro-2-bromoanilide* is readily soluble in both

alcohol and glacial acetic acid. It crystallises from acetic acid in colourless, flattened plates melting at 167·5°, which in convergent light show a positive biaxial figure, the axial angle being extremely small:

0·2149 gave 0·2002 AgCl + AgBr. Cl = 9·97; Br = 22·48.

$C_{13}H_8O_3N_2ClBr$ requires Cl = 9·97; Br = 22·48 per cent.

m-*Nitrobenzo*-2:4-*dichloroanilide* crystallises from glacial acetic acid in colourless, flattened plates melting at 183°; straight extinction. Normal to plate emerges the acute bisectrix of a positive biaxial figure; axial angle, medium:

0·2126 gave 0·1957 AgCl. Cl = 22·77.

$C_{13}H_8O_3N_2Cl_2$ requires Cl = 22·80 per cent.

p-*Nitrobenzo*-2-*chloro*-4-*bromoanilide* is moderately readily soluble in boiling glacial acetic acid, but sparingly so in boiling alcohol. On rapidly cooling a concentrated boiling alcoholic solution, it separates in tufts of very fine, almost colourless, hair-like crystals, which grow together to a felt-like mass. Among these interlaced, hair-like crystals, six-sided pale yellow plates with straight extinction almost at once make their appearance, and rapidly grow at the expense of the hair-like form, which dissolves and disappears. If the pulpy mass of fine crystals is shaken, the conversion is complete in a few minutes, the compact form subsiding as a sandy, crystalline powder melting at 199°:

0·2265 gave 0·2109 AgCl + AgBr. Cl = 9·96; Br = 22·47.

$C_{13}H_8O_3N_2ClBr$ requires Cl = 9·97; Br = 22·48 per cent.

p-*Nitrobenzo*-2:4-*dibromoanilide* is somewhat readily soluble in boiling glacial acetic acid, but less readily so in boiling alcohol. On rapidly cooling a boiling saturated alcoholic solution, it separates in very fine, hair-like crystals, which on account of their small size appear almost colourless. On allowing these to remain in the solvent at the ordinary temperature, small, pale yellow, six-sided, compact plates with straight extinction, seen under the microscope to be stout, very much flattened prisms with domed ends, make their appearance, and grow at the expense of the hair-like form, which gradually dissolves and disappears. On allowing the felted mass of the hair-like form to remain undisturbed at the ordinary temperature in a small flask, the conversion was nearly complete in about twelve hours, and all crystals of the first form had disappeared at the end of three days. Both forms melt at 194°:

0·2230 gave 0·2092 AgBr. Br = 39·92.

$C_{13}H_8O_3N_2Br_2$ requires Br = 39·96 per cent.

p-*Nitrobenzo*-4-*chloro*-2-*bromoanilide* is readily soluble in boiling

glacial acetic acid, but less readily so in boiling alcohol. On cooling a boiling saturated alcoholic solution it separates in very fine, almost colourless needles with straight extinction, which interlace, and finally completely fill the liquid. After some time pale yellow, stout, six-sided, rhombic plates (82°) with diagonal extinction make their appearance, and slowly grow at the expense of the first form, cutting their way down through the pulp-like, crystalline mass in a very characteristic manner. The conversion is complete after about three days. Both forms melt at 174°:

0·2329 gave 0·2166 AgCl + AgBr. Cl = 9·95; Br = 22·44.
$C_{13}H_8O_3N_2ClBr$ requires Cl = 9·97; Br = 22·48 per cent.

p-*Nitrobenzo*-2:4-*dichloroanilide* is readily soluble in boiling glacial acetic acid, but less readily so in boiling alcohol. On cooling a boiling saturated alcoholic solution it separates in very fine, almost colourless needles. After some hours small, four-sided, pale yellow plates make their appearance, and slowly grow, cutting their way down through the interlaced crystals of the first form, which dissolve and disappear in the neighbourhood of the growing crystals. These compact plates, when seen under the microscope, appear as faces of stout, six-sided prisms with domed ends. This transformation is slow; thus in one experiment in which a small flask half filled with a pulp of the needle-shaped form was allowed to remain undisturbed at the ordinary temperature, three weeks elapsed before all the unstable form had disappeared. The length of time taken in transforming naturally depends on the amount to be transformed, as well as on the temperature and on the nature of the solvent. Both forms melt at 174°, the unstable form transforming before the melting point is reached:

0·1725 gave 0·1574 AgCl. Cl = 22·56.
$C_{13}H_8O_3N_2Cl_2$ requires Cl = 22·80 per cent.

The 2:4-disubstituted phthalanils are easily obtained by heating together equivalent quantities of the anilines and phthalic anhydride for several hours to about 180°.

Phthalo-2-*chloro*-4-*bromoanil*, $C_6H_4<^{CO}_{CO}>N\cdot C_6H_3ClBr$, is fairly readily soluble in boiling alcohol, and readily so in boiling glacial acetic acid, from which it crystallises in colourless prisms melting at 165°; straight extinction:

0·2120 gave 0·2094 AgCl + AgBr. Cl = 10·57; Br = 23·84.
$C_{14}H_7O_2NClBr$ requires Cl = 10·54; Br = 23·75 per cent.

Phthalo-4-*chloro*-2-*bromoanil* is readily soluble in boiling glacial acetic acid, and in boiling alcohol, from either of which it crystallises in colourless prisms with straight extinction melting at 140°:

0·2299 gave 0·2267 AgCl + AgBr. Cl = 10·56; Br = 23·79.

$C_{14}H_7O_2NClBr$ requires Cl = 10·54; Br = 23·75 per cent.

Phthalo-2:4-*dichloroanil*, $C_6H_4\langle{}^{CO}_{CO}\rangle N\cdot C_6H_3Cl_2$, is fairly readily soluble in boiling alcohol, and readily so in boiling glacial acetic acid. It crystallises from either in colourless prisms melting at 155°; straight extinction:

0·2342 gave 0·2302 AgCl. Cl = 24·31.

$C_{14}H_7O_2NCl_2$ requires Cl = 24·28 per cent.

Phthalo-2:4-*dibromoanil* is fairly readily soluble in boiling alcohol, and readily so in boiling glacial acetic acid, from which it crystallises in colourless prisms melting at 153·5°; straight extinction:

0·2198 gave 0·2171 AgBr. Br = 42·03.

$C_{14}H_7O_2NBr_2$ requires Br = 41·97 per cent.

The methyl and ethyl dihalogen-substituted carbanilates are easily prepared by dissolving equivalent quantities of the corresponding aniline and of pyridine in dry ether, and adding very slowly, as the action is violent, the equivalent amount of methyl or ethyl chloroformate. The ether is then distilled off, and the solid product well washed with dilute hydrochloric acid to remove the pyridine, and crystallised from alcohol.

Methyl 2-*chloro*-4-*bromocarbanilate*, $C_6H_3ClBr\cdot NH\cdot CO_2Me$, crystallises from alcohol, in which it is very readily soluble, in colourless needles melting at 76·5°; extinction 42°:

0·2035 gave 0·2524 AgCl + AgBr. Cl = 13·28; Br = 29·93.

$C_8H_7O_2NClBr$ requires Cl = 13·40; Br = 30·22 per cent.

Ethyl 2-*chloro*-4-*bromocarbanilate*, $C_6H_3ClBr\cdot NH\cdot CO_2Et$, is readily soluble in alcohol, from which it crystallises in colourless needles melting at 96°; extinction 38°:

0·2012 gave 0·2380 AgCl + AgBr. Cl = 12·66; Br = 28·55.

$C_9H_9O_2NClBr$ requires Cl = 12·73; Br = 28·70 per cent.

Methyl 2:4-dibromocarbanilate, $C_6H_3Br_2\cdot NH\cdot CO_2Me$, has been obtained by Hentschel (*J. pr. Chem.*, [ii], 1886, **34**, 423) by direct bromination and by Fromm and Heyder (*Ber.*, 1909, **42**, 3801) by the action of bromine on phenylthiocarbimide in the presence of aqueous methyl alcohol. It is easily prepared by the general method from 2:4-dibromoaniline, and crystallises from alcohol, in which it is readily soluble, in colourless needles melting at 97°. Hentschel gives the melting point as 96·5°. (Found, Br = 51·80. Calc., Br = 51·74 per cent.)

Ethyl 2:4-dibromocarbanilate, $C_6H_3Br_2\cdot NH\cdot CO_2Et$, was prepared by Fromm and Heyder (*loc. cit.*) by the action of bromine on phenyl-

thiocarbimide in the presence of aqueous ethyl alcohol. It is easily prepared by the above method. It crystallises from alcohol, in which it is readily soluble, in colourless needles melting at 101°, with extinction 40°. (Found, Br = 49·58. Calc., Br = 49·49 per cent.)

Methyl 4-chloro-2-bromocarbanilate is very readily soluble in alcohol, from which it crystallises in colourless needles melting at 87·5°:

0·1146 gave 0·1440 AgCl + AgBr. Cl = 13·45; Br = 30·32.

$C_8H_7O_2NBrCl$ requires Cl = 13·40; Br = 30·22 per cent.

Ethyl 4-chloro-2-bromocarbanilate crystallises from alcohol, in which it dissolves very readily, in colourless needles melting at 90°:

0·1510 gave 0·1760 AgCl + AgBr. Cl = 12·48; Br = 28·13.

$C_9H_9O_2NBrCl$ requires Cl = 12·73; Br = 28·70 per cent.

Methyl 2:4-dichlorocarbanilate, $C_6H_3Cl_2\cdot NH\cdot CO_2Me$, is extremely readily soluble in alcohol, from which it crystallises in colourless needles melting at 70·5°:

0·1113 gave 0·1450 AgCl. Cl = 32·22.

$C_8H_7O_2NCl_2$ requires Cl = 32·23 per cent.

Ethyl 2:4-dichlorocarbanilate, $C_6H_3Cl_2\cdot NH\cdot CO_2Et$, crystallises from alcohol, in which it is readily soluble, in colourless needles melting at 89°:

0·1121 gave 0·1443 AgCl. Cl = 30·64.

$C_9H_9O_2NCl_2$ requires Cl = 30·30 per cent.

Like other substituted anilines, 2-chloro-4-bromoaniline and 4-chloro-2-bromoaniline react readily with carbamide at a somewhat elevated temperature, ammonia is liberated, and the mono- and *s*-di-dihalogen-substituted carbamides are produced. The latter compounds are formed in largest amount, even when a considerable excess of carbamide is used, and are easily isolated, owing to their very sparing solubility in ordinary organic solvents. A yield of the *s*-tetra-substituted carbamide amounting to about 80 per cent. of the theoretical, is obtained when a gram-molecule of the aniline is heated with 4 gram-molecules of carbamide to 180° for forty hours.

s-2:2'-Dichloro-4:4'-dibromodiphenylcarbamide,

$C_6H_3ClBr\cdot NH\cdot CO\cdot NH\cdot C_6H_3ClBr$,

is very sparingly soluble in boiling glacial acetic acid. It is much more readily soluble in hot nitrobenzene, from which it separates in colourless, very fine, hair-like needles with oblique extinction, melting at 279°:

0·1420 gave 0·2133 AgCl + AgBr. Cl = 16·08; Br = 36·25.

$C_{13}H_8ON_2Cl_2Br_2$ requires Cl = 16·16; Br = 36·42 per cent.

s-4:4′-*Dichloro*-2:2′-*dibromodiphenylcarbamide* resembles the isomeric compound very closely. It crystallises from hot nitrobenzene in colourless, fine needles melting at 274°; extinction, 40°:

0·1988 gave 0·2990 AgCl + AgBr. Cl = 16·10; Br = 36·29.
$C_{13}H_8ON_2Cl_2Br_2$ requires Cl = 16·16; Br = 36·42 per cent.

All the dihalogen-substituted anilines react readily with diethyl oxalate at a suitably high temperature; using excess of ester, the corresponding oxanilide is the chief compound; using excess of aniline, the oxanilide predominates. They are easily separated on account of the very sparing solubility of the tetra-substituted oxanilides. The 2:4-dihalogen derivatives are best prepared by heating 1 gram-molecule of the aniline with 5 gram-molecules of diethyl oxalate to about 220° for an hour. On cooling and adding a little alcohol, both the oxanilate and the tetra-substituted oxanilide separate out. A further quantity of the two compounds can be obtained by distilling off the alcohol from the filtrate and re-heating the residue.

The two compounds are readily separated by boiling with alcohol, when the oxanilate is dissolved. The yield of the tetrahalogen-substituted oxanilide is always very small.

The disubstituted oxanilic acids are best prepared by suspending the corresponding ethyl disubstituted oxanilates in about twenty times their weight of water, adding rather more than the equivalent of sodium carbonate, and passing steam until the esters have disappeared. The sodium salts of the acids crystallise out on cooling. On adding an excess of hydrochloric acid to hot aqueous solutions of the salts, and cooling, the acids separate. They crystallise from water with one molecule of water of crystallisation. When the monohydrated acids are dehydrated and recrystallised from toluene or benzene the anhydrous acids are obtained.

The disubstituted oxanilamides separate as sparingly soluble, crystalline solids when dry gaseous ammonia is passed into warm alcoholic solutions of the corresponding ethyl oxanilates.

Ethyl 2-*chloro*-4-*bromo-oxanilate*, $C_6H_3ClBr{\cdot}NH{\cdot}CO{\cdot}CO_2Et$, is readily soluble in boiling alcohol, from which it crystallises in colourless needles melting at 124°:

0·1700 gave 0·1828 AgCl + AgBr. Cl = 11·51; Br = 25·95.
$C_{10}H_9O_3NClBr$ requires Cl = 11·57; Br = 26·08 per cent.

2-*Chloro*-4-*bromo-oxanilic acid*, $C_6H_3ClBr{\cdot}NH{\cdot}CO{\cdot}CO_2H$, crystallises in colourless needles melting and decomposing at 131°:

0·1115 gave 0·1332 AgCl + AgBr. Cl = 12·79; Br = 28·83.
$C_8H_5O_3NClBr$ requires Cl = 12·73; Br = 28·70 per cent.

s-2:2'-*Dichloro*-4:4'-*dibromo-oxanilide*,

$$C_6H_3ClBr\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_3ClBr,$$

is sparingly soluble in boiling alcohol or glacial acetic acid, but dissolves readily in hot nitrobenzene, from which it crystallises in small, colourless needles melting at 285°:

0·0727 gave 0·1026 AgCl + AgBr. Cl = 15·11; Br = 34·06.

$C_{14}H_8O_2N_2Cl_2Br_2$ needs Cl = 15·19; Br = 34·23 per cent.

2-*Chloro*-4-*bromo-oxanilamide*, $C_6H_3ClBr\cdot NH\cdot CO\cdot CO\cdot NH_2$, is moderately readily soluble in boiling alcohol, and readily so in hot nitrobenzene. It crystallises in colourless needles melting at 243°:

0·0905 gave 0·1079 AgCl + AgBr. Cl = 12·76; Br = 28·77.

$C_8H_6O_2N_2ClBr$ requires Cl = 12·78; Br = 28·80 per cent.

Ethyl 4-*chloro*-2-*bromo-oxanilate* crystallises from alcohol, in which it is readily soluble, in colourless needles melting at 121°:

0·1932 gave 0·2087 AgCl + AgBr. Cl = 11·56; Br = 26·07.

$C_{10}H_9O_3NClBr$ requires Cl = 11·57; Br = 26·08 per cent.

4-*Chloro*-2-*bromo-oxanilic acid* crystallises from boiling benzene in colourless needles melting with decomposition at 126—127°:

When crystallised from water it separates in colourless needles containing one molecule of water of crystallisation:

0·1177 gave 0·1320 AgCl + AgBr. Cl = 12·00; Br = 27·06.

$C_8H_5O_3NClBr,H_2O$ requires Cl = 11·96; Br = 26·96 per cent.

s-4:4'-*Dichloro*-2:2'-*dibromo-oxanilide* is very sparingly soluble in boiling glacial acetic acid. It crystallises from hot nitrobenzene, in which it is fairly readily soluble, in small, colourless needles melting at 295°:

0·1531 gave 0·2159 AgCl + AgBr. Cl = 15·10; Br = 34·03.

$C_{14}H_8O_2N_2Cl_2Br_2$ requires Cl = 15·19; Br = 34·23 per cent.

4-*Chloro*-2-*bromo-oxanilamide* crystallises from alcohol in colourless needles melting at 236°:

0·1658 gave 0·1963 AgCl + AgBr. Cl = 12·68; Br = 28·57.

$C_8H_6O_2N_2ClBr$ requires Cl = 12·78; Br = 28·80 per cent.

Ethyl 2:4-*dibromo-oxanilate*, $C_6H_3Br_2\cdot NH\cdot CO\cdot CO_2Et$, is readily soluble in hot alcohol, from which it separates in colourless, curved, hair-like crystals melting at 130°:

0·1750 gave 0·1870 AgBr. Br = 45·47.

$C_{10}H_9O_3NBr_2$ requires Br = 45·51 per cent.

2:4-*Dibromo-oxanilic acid*, $C_6H_3Br_2\cdot NH\cdot CO\cdot CO_2H$, crystallises from boiling benzene in colourless needles melting and decomposing at 138° into carbon dioxide and 2:4-dibromoformanilide. It crystallises from boiling water, in which it is readily soluble, in slender,

colourless prisms, containing one molecule of water of crystallisation, which is slowly lost at 100°:

0·1711 gave 0·1898 AgBr. Br = 47·20.

$C_8H_5O_3NBr_2,H_2O$ requires Br = 46·88 per cent.

2:4:2′:4′-*Tetrabromo-oxanilide*,

$C_6H_3Br_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_3Br_2$,

is very sparingly soluble in boiling glacial acetic acid, 150 c.c. dissolving only about 0·1 gram. It is moderately readily soluble in boiling nitrobenzene, from which it crystallises in colourless needles melting at 298°; straight extinction:

0·2955 gave 0·3984 AgBr. Br = 57·37.

$C_{14}H_8O_2N_2Br_4$ requires Br = 57·52 per cent.

2:4-*Dibromo-oxanilamide*, $C_6H_3Br_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, crystallises from alcohol in colourless needles melting at 250°:

0·2604 gave 0·3018 AgBr. Br = 49·32.

$C_8H_6O_2N_2Br_2$ requires Br = 49·66 per cent.

It has been shown (Chattaway and Mason, T., 1910, **97**, 339) that diethyl malonate at its boiling point reacts with the halogen-substituted anilines, halogen derivatives of malonanilide and of ethyl malonanilate being produced. These can be separated owing to the sparing solubility of the substituted malonanilides and the ready solubility of the ethyl malonanilates in all ordinary solvents. The halogen-substituted malonanilic acids are also very easily obtained by hydrolysing the substituted malonanilic esters, by suspending them in a dilute solution of sodium carbonate and passing steam through the liquid until the ester disappears. After concentrating the solutions and adding a slight excess of hydrochloric acid, the acids separate in a crystalline state. When heated, the malonanilic acids decompose quantitatively into carbon dioxide and the corresponding substituted acetanilide. The malonanilamides are obtained by passing ammonia into alcoholic solutions of the corresponding ethyl malonanilates.

2:2′-*Dichloro*-4:4′-*dibromomalonanilide*,

$C_6H_3ClBr{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_3ClBr$,

is sparingly soluble in boiling alcohol, and moderately readily so in boiling glacial acetic acid, from which it crystallises in colourless needles, with straight extinction, melting at 214°:

0·1964 gave 0·2700 AgCl + AgBr. Cl = 14·72; Br = 33·18.

$C_{15}H_{10}O_2N_2Cl_2Br_2$ requires Cl = 14·74; Br = 33·24 per cent.

Ethyl 2-*chloro*-4-*bromomalonanilate*,

$C_6H_3ClBr{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$,

is very readily soluble in hot alcohol, from which it crystallises in

colourless, prismatic plates, with straight extinction, melting at 81·5°:

0·1990 gave 0·2061 AgCl + AgBr. Cl = 11·09; Br = 24·99.

$C_{11}H_{11}O_3NClBr$ requires Cl = 11·06; Br = 24·94 per cent.

2-Chloro-4-bromomalonanilic acid, $C_6H_3ClBr{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, crystallises well from hot water or alcohol, in both of which it is readily soluble, in long, slender, colourless prisms. When quickly heated it melts at 165° and evolves carbon dioxide, producing aceto-2-chloro-4-bromoanilide:

0·1598 gave 0·1799 AgCl + AgBr. Cl = 12·05; Br = 27·17.

$C_9H_7O_3NClBr$ requires Cl = 12·12; Br = 27·33 per cent.

2-Chloro-4-bromomalonanilamide,

$$C_6H_3ClBr{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH_2,$$

is readily soluble in alcohol, from which it crystallises in long, slender, colourless needles melting at 149°:

0·0872 gave 0·0994 AgCl + AgBr. Cl = 12·20; Br = 27·51.

$C_9H_8O_2N_2ClBr$ requires Cl = 12·16; Br = 27·42 per cent.

4:4′-Dichloro-2:2′-dibromomalonanilide crystallises from boiling glacial acetic acid, in which it is moderately readily soluble, in colourless prisms melting at 221°, with straight extinction, in convergent light an acute bisectrix of a wide angle positive biaxial figure almost normal, axial plane parallel to elongation of plate:

0·2342 gave 0·3206 AgCl + AgBr. Cl = 14·65; Br = 33·03.

$C_{15}H_{10}O_2N_2Cl_2Br_2$ requires Cl = 14·74; Br = 33·24 per cent.

Ethyl 4-chloro-2-bromomalonanilate is very readily soluble in alcohol, from which it separates in colourless, prismatic plates melting at 83·5°:

0·1675 gave 0·1740 AgCl + AgBr. Cl = 11·12; Br = 25·07.

$C_{11}H_{11}O_3NClBr$ requires Cl = 11·06; Br = 24·93 per cent.

4-Chloro-2-bromomalonanilic acid crystallises from hot water, in which it is readily soluble, in long, colourless prisms. It melts, when quickly heated, at 161°, giving off carbon dioxide and producing aceto-4-chloro-2-bromoanilide:

0·1143 gave 0·1290 AgCl + AgBr. Cl = 12·08; Br = 27·23.

$C_9H_7O_3NClBr$ requires Cl = 12·12; Br = 27·33 per cent.

4-Chloro-2-bromomalonanilamide crystallises from alcohol, in which it is very readily soluble, in long, slender, colourless needles melting at 159°.

2:4-*Dibromomalonanilamide*, $C_6H_3Br_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, is very readily soluble in alcohol, and crystallises in colourless, slender needles melting at 164°: .

0·1374 gave 0·1545 AgBr. Br = 47·85.

$C_9H_8O_2N_2Br_2$ requires Br = 47·58 per cent.

The dihalogen-substituted sulphonanilides are readily obtained by dissolving the aniline mixed with an equivalent weight of pyridine in dry ether, and adding an ethereal solution of the equivalent amount of the sulphonyl chloride. The ether is expelled on the water-bath, and the product washed with dilute hydrochloric acid, and crystallised from alcohol or acetic acid.

They are stable, well-crystallised compounds, which react with hypochlorous and hypobromous acids to yield stable *N*-chlorides and bromides.

Benzenesulphon-2-chloro-4-bromoanilide,

$$C_6H_3ClBr\cdot NH\cdot SO_2\cdot C_6H_5,$$

crystallises from hot alcohol, in which it is very readily soluble, in striated, colourless, flat prisms, with straight extinction, melting at 122°:

It was analysed by conversion into its *N*-chloride and titration of the iodine liberated, when a weighed amount of the compound dissolved in chloroform is added to a solution of potassium iodide acidified with acetic acid.

Benzenesulphon-2-chloro-4-bromophenylchloroamide,

$$C_6H_3ClBr\cdot NCl\cdot SO_2\cdot C_6H_5,$$

crystallises from a mixture of chloroform and light petroleum in colourless, stout prisms. When rapidly heated it melts at 111—112°:

0·6272 liberated I = 30·6 c.c. *N*/10-I. Cl as NCl = 9·14.

$C_{12}H_8O_2NCl_2BrS$ requires Cl as NCl = 9·30 per cent.

Benzenesulphon-4-chloro-2-bromoanilide is very readily soluble in glacial acetic acid or alcohol, from which it crystallises in colourless, flat prisms, terminated by domes with straight extinction melting at 128°:

Benzenesulphon-4-chloro-2-bromophenylchloroamide crystallises in colourless, stout prisms. When rapidly heated it melts at 123°:

0·5133 liberated I = 26·6 c.c. *N*/10-I. Cl as NCl = 9·18.

$C_{12}H_8O_2NCl_2BrS$ requires Cl as NCl = 9·30 per cent.

p-*Toluenesulphon-2-chloro-4-bromoanilide*,

$$C_6H_3ClBr\cdot NH\cdot SO_2\cdot C_6H_4Me,$$

is readily soluble in alcohol, and crystallises in colourless plates melting at 121°.

p-*Toluenesulphon-2-chloro-4-bromophenylchloroamide*,

$$C_6H_3ClBr\cdot NCl\cdot SO_2\cdot C_6H_4Me,$$

is very readily soluble in chloroform, from which it separates as the solvent evaporates in colourless, stout, prismatic crystals melting at 78°:

0·1572 liberated I = 7·8 c.c. *N*/10-I. Cl as NCl = 8·79.

$C_{13}H_{10}O_2NCl_2BrS$ requires Cl as NCl = 8·97 per cent.

p-*Toluenesulphon*-2:4-*dibromoanilide*,

$$C_6H_3Br_2\cdot NH\cdot SO_2\cdot C_6H_4Me,$$

crystallises from alcohol, in which it is readily soluble, in colourless plates, with straight extinctions melting at 134°:

p-*Toluenesulphon*-2:4-*dibromophenylchloroamide*,

$$C_6H_3Br_2\cdot NCl\cdot SO_4\cdot C_6H_4Me,$$

crystallises from chloroform, in which it is very readily soluble, in colourless, stout prisms, melting at 78°:

0·1484 liberated I = 6·95 c.c. *N*/10-I. Cl as NCl = 8·30.
$C_{13}H_{10}O_2NCl_2Br_2S$ requires Cl as NCl = 8·07 per cent.

p-*Toluenesulphon*-4-*chloro*-2-*bromoanilide* crystallises from alcohol, in which it is very readily soluble, in colourless plates melting at 126·5°.

p-*Toluenesulphon*-4-*chloro*-2-*bromophenylchloroamide* is very readily soluble in chloroform, and separates as the solvent evaporates, in colourless, stout prisms melting at 77°.

p-*Nitrotoluene*-o-*sulphon*-2-*chloro*-4-*bromoanilide*,

$$C_6H_3ClBr\cdot NH\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

is moderately readily soluble in alcohol, and readily so in boiling glacial acetic acid, from which it crystallises in very pale yellow, obliquely terminated prisms, melting at 164·5°; extinction, 25°.

p-*Nitrotoluene*-o-*sulphon*-2-*chloro*-4-*bromophenylchloroamide*,

$$C_6H_3ClBr\cdot NCl\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

crystallises in colourless prisms, which, when rapidly heated, melt at 123—124°:

0·5084 liberated I = 22·6 c.c. *N*/10-I. Cl as NCl = 7·86.
$C_{13}H_9O_4N_2Cl_2BrS$ requires Cl as NCl = 8·05 per cent.

p-*Nitrotoluene*-o-*sulphon*-4-*chloro*-2-*bromoanilide* is moderately readily soluble in alcohol or glacial acetic acid, and crystallises in very pale yellow, flattened prisms, with 60° and 43° terminal faces, and straight extinction melting at 165°.

p-*Nitrotoluene*-o-*sulphon*-4-*chloro*-2-*bromophenylchloroamide* crystallises in colourless prisms, melting at 122° when quickly heated:

0·4230 liberated I = 18·8 c.c. *N*/10-I. Cl as NCl = 7·88.
$C_{13}H_9O_4N_2Cl_2BrS$ requires Cl as NCl = 8·05 per cent.

p-*Nitrotoluene*-o-*sulphon*-2:4-*dibromoanilide*,

$$C_6H_3Br_2\cdot NH\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

is moderately readily soluble in alcohol, and readily so in glacial acetic acid. It crystallises in very faintly yellow, flat prisms with straight extinction melting at 173°.

p-*Nitrotoluene*-o-*sulphon*-2:4-*dibromophenylchloroamide*,

$$C_6H_3Br_2\cdot NCl\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

crystallises in colourless prisms melting at 124—125° when quickly heated:

0·2839 liberated I = 11·4 c.c. *N*/10-I. Cl as NCl = 7·12.
$C_{13}H_9O_4N_2ClBr_2S$ requires Cl as NCl = 7·32 per cent.

All the dihalogen-substituted anilines yield diazonium salts, which couple readily in alkaline solution with β-naphthol. Several of these compounds are described, as they are useful for purposes of identification.

2-Chloro-4-bromobenzeneazo-β-naphthol, $C_6H_3ClBr{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$, is moderately readily soluble in glacial acetic acid, from which it crystallises in plates melting at 210°, which have a beetle-green colour by reflected light and a red colour in transmitted light:

0·1946 gave 0·1769 AgCl + AgBr. Cl = 9·73; Br = 21·93.
$C_{16}H_{10}ON_2ClBr$ requires Cl = 9·80; Br = 22·10 per cent.

4-Chloro-2-bromobenzeneazo-β-naphthol crystallises from glacial acetic acid in brilliant red plates melting at 193°; they give straight extinction, and are sharply pleochroic-orange-red:

0·1516 gave 0·1383 AgCl + AgBr. Cl = 9·76; Br = 22·01.
$C_{16}H_{10}ON_2ClBr$ requires Cl = 9·80; Br = 22·10 per cent.

2:4-Dibromobenzeneazo-β-naphthol has already been described by Hantzsch and Schmiedel (*Ber.*, 1897, **30**, 78). It is sparingly soluble in acetic acid, from which it crystallises in flattened, brick-red prisms, melting at 203°. They give straight extinction, and in convergent light a biaxial figure is visible. (Found, Br = 39·19. $C_{16}H_{10}ON_2Br_2$ requires Br = 39·38 per cent.)

The authors wish to express their thanks to Mr. T. V. Barker, who has kindly described the crystals.

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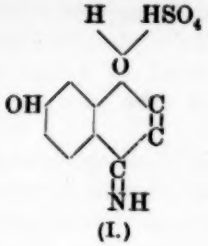
OXFORD. [*Received, December 14th*, 1915].

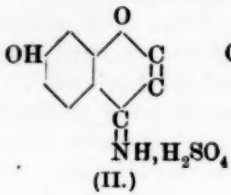
IX.—*A Synthesis of Flavones.*

By BROJENDRA NATH GHOSH.

IT has been shown (Jacobson and Ghosh, T., 1915, **107**, 1051) that the condensation of ethyl α-phenylacetoacetate with phenols leads to the production of substituted γ-benzopyrones or flavones.

It is shown in the present paper that if, instead of the ester, the


(I.)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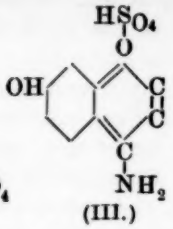
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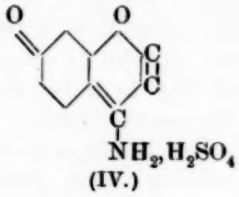
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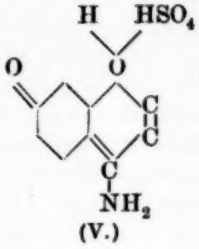
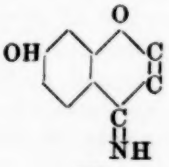
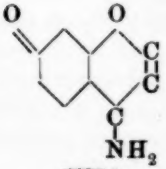

(V.)

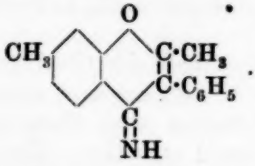
and those of the free bases by


(VI.)

or


(VII.)

Forms I, II, and III should all yield a base of the constitution shown in VI. Forms I, II, and VI may at once be rejected because they do not contain any quinonoid arrangement. Any one of the formulæ represented by III, IV, or V may represent the structure of the salts, and in the free state VII ought to be the proper representation of the compounds because they all contain the quinonoid arrangement. In order to test this view, *m*-cresol was condensed with acetylphenylacetonitrile, and the free base obtained from this condensation was found to be quite colourless. In this case the base must have the structure



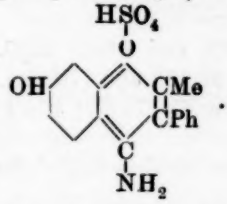
No quinonoid arrangement is possible here, and the absence of colour is in accordance with the view that the coloured compounds

have the quinonoid structure. This substance dissolves in concentrated sulphuric acid with a yellow colour, and gives a yellow sulphate, and therefore the constitution of this salt must be represented by III. Thus it becomes evident that formula III ought to be the proper representation of the salts, whilst when they are converted into their bases rearrangement into the quinonoid structure (VII) takes place when a hydroxyl group is present, but they retain their structure (VI) when no such arrangement is possible.

Experimental.

Condensations with Acetylphenylacetonitrile.

4-Imino-7-hydroxy-3-phenyl-2-methyl-γ-benzopyran Sulphate,



Concentrated sulphuric acid (15 c.c.) was slowly added to resorcinol (4 grams) and acetylphenylacetonitrile (5 grams) (Beckh, *Ber.*, 1898, **31**, 3161). When kept overnight, the crystalline mass obtained from the cooled solution was poured on ice. After three hours the clear solution yielded a voluminous, crystalline precipitate, which was crystallised from very dilute sulphuric acid. The yield was almost quantitative:

0·1302 gave 0·2630 CO_2 and 0·0538 H_2O. C = 55·10; H = 4·59.
0·1715 „ 6·4 c.c. N_2 at 21° and 768 mm. N = 4·23.
$C_{16}H_{13}O_2N,H_2SO_4$ requires C = 55·01; H = 4·50; N = 4·00 per cent.

The salt forms short, yellow needles, melting to a dark red liquid at 246°; it dissolves in dilute sodium hydroxide solution and in concentrated sulphuric acid to yellow solutions, the latter showing a green fluorescence, which is also exhibited in dilute alcoholic solution. Alcoholic ferric chloride develops a violet coloration.

The *base*, prepared by treating an alcoholic solution of the sulphate with an excess of aqueous sodium acetate, crystallised from dilute alcohol in brown prisms, melting and decomposing at 221°:

0·1214 gave 0·3300 CO_2 and 0·0628 H_2O. C = 74·15; H = 5·55.
0·0980 „ 4·8 c.c. N_2 at 15° and 752 mm. N = 5·67.
$C_{16}H_{13}O_2N,\frac{1}{2}H_2O$ requires C = 73·85; H = 5·38; N = 5·38 per cent.

The *picrate* separated in orange yellow needles, melting at 227°:

0·0760 gave 8·6 c.c. N_2 at 17° and 764 mm. N = 11·66.

$C_{16}H_{13}O_2N,C_6H_3O_7N_3$ requires N = 11·66 per cent.

The *perchlorate* separated in yellow needles, which on heating decomposed with explosive violence:

0·1232 required 3·5 c.c. *N*/10-NaOH. $HClO_4$ = 28·4.

$C_{16}H_{13}O_2N,HClO_4$ requires $HClO_4$ = 28·5 per cent.

The *acetyl* derivative crystallised from very dilute alcohol in very faintly yellow needles, melting at 135°. It dissolved in concentrated sulphuric acid with a yellow colour:

0·1138 gave 0·2992 CO_2 and 0·0526 H_2O. C = 71·70; H = 5·13.

0·1150 „ 4·3 c.c. N_2 at 17° and 764 mm. N = 4·71.

$C_{18}H_{15}O_3N,\frac{1}{2}H_2O$ requires C = 71·52; H = 5·30; N = 4·70 per cent.

The *benzoyl* derivative crystallised from alcohol in colourless needles, melting at 178—179°:

0·1104 gave 0·3070 CO_2 and 0·0467 H_2O. C = 75·84; H = 4·71.

0·1860 „ 6 c.c. N_2 at 16° and 770 mm. N = 3·81.

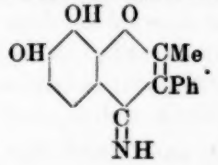
$C_{23}H_{17}O_3N,\frac{1}{2}H_2O$ requires C = 75·80; H = 4·94; N = 3·84 per cent.

Reaction with Dilute Sulphuric Acid.

In order to prove the constitution, 2 grams of the above sulphate were boiled under reflux with about 30 c.c. of 10 per cent. sulphuric acid for two hours. The clear solution yielded an oil, which solidified to a pale yellow, crystalline mass. This was collected while hot, washed with hot water, and crystallised from alcohol, when it separated in colourless needles, melting at 224—225° (the melting point of 7-hydroxy-3-phenyl-2-methyl-γ-benzopyrone is 226°; Jacobson and Ghosh, *loc. cit.*). The substance developed a bluish-violet fluorescence in sulphuric acid, whilst the imine gave a green fluorescence with sulphuric acid.

The dilute sulphuric acid, after the precipitate had been removed, was boiled with excess of sodium hydroxide, when ammonia was evolved, showing that the imine had been hydrolysed.

4-Imino-7:8-dihydroxy-3-phenyl-2-methyl-γ-benzopyran,



This was prepared from pyrogallol (4 grams), acetylphenylacetonitrile (5 grams), and concentrated sulphuric acid (15 c.c.). The alcoholic solution of the yellow substance obtained was treated with

an excess of aqueous sodium acetate, and the base was crystallised from dilute alcohol:

0·1243 gave 0·3178 CO_2 and 0·0556 H_2O. C = 69·73; H = 4·97.
0·0936 „ 4 c.c. N_2 at 19° and 764 mm. N = 4·93.
$C_{16}H_{13}O_3N,\frac{1}{2}H_2O$ requires C = 69·56; H = 5·07; N = 5·07 per cent.

The compound forms dark brown prisms, which shrink at 125° and melt and decompose at 142°; it gives a green colour with alcoholic ferric chloride, reduces ammoniacal silver nitrate on warming, and gives a brown sodium salt with sodium hydroxide solution.

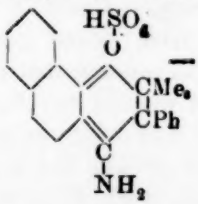
The *acetyl* derivative crystallises from alcohol in pale yellow needles, melting at 194°:

0·1271 gave 0·3176 CO_2 and 0·0540 H_2O. C = 68·18; H = 4·72.
0·1016 „ 3·6 c.c. N_2 at 15° and 766 mm. N = 4·18.
$C_{20}H_{17}O_5N$ requires C = 68·37; H = 4·84; N = 3·98 per cent.

Reaction with Dilute Sulphuric Acid.

Two grams of the above base were boiled with 25 c.c. of 10 per cent. sulphuric acid for four hours. The substance which separated crystallised from acetic acid in yellow prisms, melting at 268°; the acetyl derivative melted at 212° (the melting point of 7:8-dihydroxy-3-phenyl-2-methyl-γ-benzopyrone is 268° and that of the acetyl derivative 210°).

4-Imino-3-phenyl-2-methyl-1:4-α-naphthapyran Sulphate,



This was prepared from α-naphthol (3 grams), acetylphenylacetonitrile (5 grams), and concentrated sulphuric acid (10 c.c.). On pouring the mixture on ice, the product separated as a viscous mass, which solidified under water. It crystallised from acetic acid containing dilute sulphuric acid in bright, orange needles, melting and decomposing at 174°:

0·1164 gave 0·2668 CO_2 and 0·0460 H_2O. C = 62·51; H = 4·40.
$C_{20}H_{15}ON,H_2SO_4$ requires C = 62·66; H = 4·43 per cent.

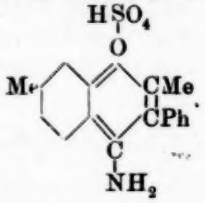
The *base*, prepared in the usual way, crystallised from dilute alcohol in pale brown prisms, melting at 162°:

0·1172 gave 0·3503 CO_2 and 0·0585 H_2O. C=81·52; H=5·55.
0·0966 „ 4·1 c.c. N_2 at 19° and 764 mm. N=4·90.
$C_{20}H_{15}ON,\frac{1}{2}H_2O$ requires C=81·63; H=5·44; N=4·76 per cent.

Reaction with Dilute Sulphuric Acid.

One gram of the naphthapyran sulphate was boiled for three hours with 10 c.c. of 10 per cent. sulphuric acid. The product crystallised from alcohol in lemon-yellow needles, melting at 209° (the melting point of 3-phenyl-2-methyl-1:4-α-naphthapyrone is 209°; Jacobson and Ghosh, *loc. cit.*).

4-Imino-3-phenyl-2:7-dimethyl-γ-benzopyran Sulphate,



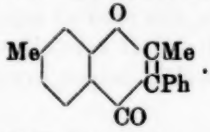
This was prepared from 4 grams of *m*-cresol, 5 grams of acetylphenylacetonitrile, and 15 c.c. of concentrated sulphuric acid. The semi-solid mass obtained on pouring the mixture on ice was dissolved in acetic acid and precipitated with dilute sulphuric acid, when it separated in yellow prisms, melting and decomposing at 122°. The yield was small:

0·1152 gave 0·2484 CO_2 and 0·0489 H_2O. C=58·80; H=4·71.
$C_{17}H_{15}ON,H_2SO_4$ requires C=58·78; H=4·89 per cent.

The *base* crystallised from dilute alcohol in short, colourless needles melting at 89°. In concentrated sulphuric acid it dissolved with a yellow colour, but without any fluorescence:

0·1054 gave 0·3168 CO_2 and 0·0574 H_2O. C=81·97; H=6·05.
0·1017 „ 5 c.c. N_2 at 20° and 764 mm. N=5·65.
$C_{17}H_{15}ON$ requires C=81·92; H=6·02; N=5·62 per cent.

3-Phenyl-2:7-dimethyl-2-benzopyrone,



Two grams of the above sulphate were boiled with 20 c.c. of 10 per cent. sulphuric acid for four hours. After cooling, the solid substance was crystallised from alcohol, from which it separated in colourless needles melting at 155°:

0·1206 gave 0·3610 CO_2 and 0·0631 H_2O. C = 81·63; H = 5·81.
$C_{17}H_{14}O_2$ requires C = 81·60; H = 5·60 per cent.

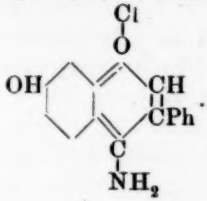
The compound is readily soluble in alcohol, benzene, or acetic acid, sparingly so in light petroleum, and insoluble in water. In concentrated sulphuric acid it dissolves to a colourless solution, but develops a bright blue fluorescence.

Condensations with Formylphenylacetonitrile.

Preparation of Formylphenylacetonitrile.

Ethyl formate (40 grams) was added in small portions at a time to a well-cooled solution of phenylacetonitrile (58·5 grams) and sodium (11·5 grams) in alcohol, when a gelatinous precipitate separated, which after keeping at the ordinary temperature for one hour was boiled on a water-bath for two hours. Alcohol was then removed, as far as possible, by distillation. The residue was dissolved in water, and after the removal of unchanged phenylacetonitrile with ether, was acidified, when formylphenylacetonitrile separated as a colourless, crystalline mass. The yield of the pure product was about 90 per cent. of the theoretical (compare Walther and Schickler, *J. pr. Chem.*, 1897, [ii], **55**, 308).

4-Imino-7-hydroxy-3-phenyl-γ-benzopyran Hydrochloride,



Phosphoryl chloride (20 c.c.) was added to resorcinol (3 grams) and formylphenylacetonitrile (4 grams) when the reaction started slowly at the ordinary temperature. The mixture, which reacted vigorously on warming at 50°, was cooled and treated with powdered ice. The yellow, granular mass crystallised from acetic acid containing dilute hydrochloric acid in short, dull yellow needles melting and decomposing at 215° after shrinking at 205°. The yield was almost quantitative:

0·1100 gave 0·2484 CO_2 and 0·0466 H_2O. C = 61·58; H = 4·70.
0·1338 .. 5·6 c.c. N_2 at 20° and 768 mm. N = 4·64.
$C_{15}H_{11}O_2N,HCl,H_2O$ requires C = 61·85; H = 4·81;
N = 4·81 per cent.

The salt gives a violet colour with alcoholic ferric chloride and

dissolves in aqueous sodium hydroxide, giving a yellowish-brown solution which evolves ammonia on warming.

The *base* crystallised from dilute alcohol in bright yellow needles melting at 226°:

0·1020 gave 0·2631 CO_2 and 0·0478 H_2O. C = 70·32; H = 5·20.
0·1254 „ 6·2 c.c. N_2 at 20° and 764 mm. N = 5·68.
$C_{15}H_{11}O_2N,H_2O$ requires C = 70·54; H = 5·09; N = 5·49 per cent.

The *acetyl* derivative crystallises from alcohol in colourless needles melting and decomposing at 186°:

0·1058 gave 0·2840 CO_2 and 0·0438 H_2O. C = 73·20; H = 4·60.
$C_{17}H_{13}O_3N$ requires C = 73·11; H = 4·66 per cent.

The *benzoyl* derivative crystallises from light petroleum in colourless needles melting at 136°:

0·1060 gave 0·2862 CO_2 and 0·0458 H_2O. C = 73·63; H = 4·80.
0·1740 „ 6 c.c. N_2 at 16° and 770 mm. N = 4·07.
$C_{22}H_{15}O_3N,H_2O$ requires C = 73·73; H = 4·93; N = 3·90 per cent.

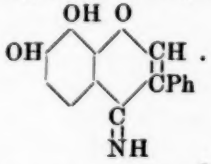
The *perchlorate* separates in bright yellow needles:

0·1222 required 3·6 c.c. *N*/10-NaOH. $HClO_4$ = 29·4.
$C_{15}H_{11}O_2N,HClO_4$ requires $HClO_4$ = 29·6 per cent.

Reaction with Dilute Sulphuric Acid.

Two grams of the above hydrochloride were boiled with 20 c.c. of 10 per cent. sulphuric acid for three hours. The product crystallised from dilute alcohol in pale yellow needles melting at 130° (the melting point of 7-hydroxy-3-phenyl-γ-benzopyrone is 131°, Jacobson and Ghosh, *loc. cit.*).

4-*Imino*-7 : 8-*dihydroxy*-3-*phenyl*-γ-*benzopyran*,



Four grams of pyrogallol, 4 grams of formylphenylacetonitrile, and 20 c.c. of phosphoryl chloride were heated at 50—60° for half an hour. The alcoholic solution of the yellow product was treated with an excess of aqueous sodium acetate and the precipitate crystallised from dilute acetic acid, from which it separated in yellow needles melting at 220° after shrinking at 208°:

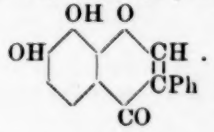
0·1009 gave 0·2462 CO_2 and 0·0459 H_2O. C = 66·54; H = 5·06.
0·3000 „ 13·4 c.c. N_2 at 18° and 764 mm. N = 5·15.
$C_{15}H_{11}O_3N,H_2O$ requires C = 66·42; H = 4·79; N = 5·16 per cent.

The compound gives a green colour with alcoholic ferric chloride and reduces ammoniacal silver nitrate solution on warming.

The *acetyl* derivative crystallised from dilute alcohol in almost colourless needles melting at 171°:

0·1001 gave 0·2354 CO_2 and 0·0418 H_2O. C = 64·13; H = 4·63.
0·2448 „ 8 c.c. N_2 at 15° and 764 mm. N = 4·19.
$C_{19}H_{15}O_5N,H_2O$ requires C = 64·22; H = 4·78; N = 3·94 per cent.

7:8-*Dihydroxy*-3-*phenyl*-γ-*benzopyrone*,



Three grams of 4-imino-7:8-dihydroxy-3-phenyl-γ-benzopyran were boiled under reflux with 30 c.c. of 10 per cent. sulphuric acid for three hours. The product crystallised from dilute alcohol in pale yellow needles melting at 215°:

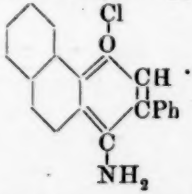
0·1194 gave 0·2729 CO_2 and 0·0489 H_2O. C = 62·29; H = 4·55.
$C_{15}H_{10}O_4,2H_2O$ requires C = 62·07; H = 4·82 per cent.

The compound is soluble in aqueous sodium hydroxide, giving a brown solution. In concentrated sulphuric acid it gives a yellow solution and develops a green fluorescence. It reduces ammoniacal silver nitrate solution on warming.

The *acetyl* derivative crystallised from alcohol in colourless needles melting at 184°. It was also prepared by boiling the imino-compound with acetic anhydride and fused sodium acetate:

0·1049 gave 0·2510 CO_2 and 0·0432 H_2O. C = 64·38; H = 4·57.
$C_{19}H_{14}O_6,H_2O$ requires C = 64·04; H = 4·49 per cent.

4-*Imino*-3-*phenyl*-1:4-α-*naphthapyran Hydrochloride*,



This was prepared by passing a current of dry hydrogen chloride into a well-cooled solution of 3 grams of α-naphthol and 3 grams of formylphenylacetonitrile in 6 c.c. of glacial acetic acid for about an hour. The product after two days was precipitated with dilute hydrochloric acid, and was crystallised from acetic acid

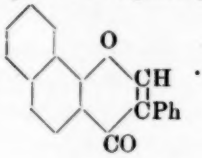
containing hydrochloric acid, from which it separated in yellow needles melting and decomposing at 135°:

0·1184 gave 0·3044 CO_2 and 0·0533 H_2O. C=70·11; H=5·01.
$C_{19}H_{13}ON,HCl,H_2O$ requires C=70·15; H=4·92 per cent.

The *base* crystallised from alcohol in dull yellow prisms which decomposed at 115—130°. In dilute alcoholic solution it gave a green fluorescence:

0·1272 gave 0·3760 CO_2 and 0·0626 H_2O. C=78·68; H=5·47.
0·1680 „ 7·4 N_2 at 20° and 764 mm. N=5·03.
$C_{19}H_{13}ON,H_2O$ requires C=78·89; H=5·19; N=4·84 per cent.

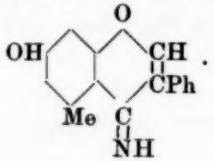
3-Phenyl-1:4-α-naphthapyrone,



This substance, prepared in the usual way from the imino-compound, crystallised from alcohol in pale yellow needles melting at 169—170°. In concentrated sulphuric acid it dissolved with a yellow colour and developed a dark green fluorescence:

0·1094 gave 0·3264 CO_2 and 0·0470 H_2O. C=81·36; H=4·77.
$C_{19}H_{12}O_2,\frac{1}{2}H_2O$ requires C=81·14; H=4·63 per cent.

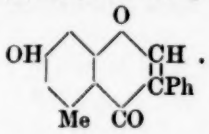
4-Imino-7-hydroxy-3-phenyl-5-methyl-γ-benzopyran,



The product obtained by warming orcinol (2 grams), formylphenylacetonitrile (2 grams), and phosphoryl chloride (20 c.c.), and then treating the alcoholic solution with an excess of aqueous sodium acetate, crystallises from alcohol in bright yellow needles which shrink at 227°, melt at 235°, and decompose at 241°. It gives a yellowish-green colour with alcoholic ferric chloride:

0·1006 gave 0·2630 CO_2 and 0·0486 H_2O. C=71·30; H=5·36.
0·1308 „ 6·2 c.c. N_2 at 20° and 760 mm. N=5·43.
$C_{16}H_{12}O_2N,H_2O$ requires C=71·64; H=5·22; N=5·22 per cent.

7-Hydroxy-3-phenyl-5-methyl-γ-benzopyrone,



This substance crystallised from alcohol in pale yellow needles melting at 224° after shrinking at 218°. In concentrated sulphuric acid it dissolved with a yellow colour and developed a dark green fluorescence. With ferric chloride it gave no coloration:

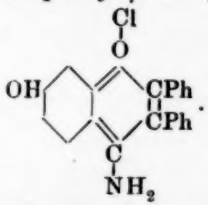
0·1402 gave 0·3418 CO_2 and 0·0696 H_2O. C = 66·48; H = 5·51.
$C_{16}H_{12}O_3,2H_2O$ requires C = 66·66; H = 5·55 per cent.

Condensations with Benzoylphenylacetonitrile.

Preparation of Benzoylphenylacetonitrile.

This was prepared in the same way as formylphenylacetonitrile from 11·5 grams of sodium dissolved in alcohol, 58 grams of phenylacetonitrile, and 75 grams of ethyl benzoate. The addition of ethyl benzoate must be gradual, and the mixture must be shaken vigorously after each addition. The yield was about 45 per cent. of the theoretical. Walther and Schickler (*loc. cit.*) by using sodium methoxide free from alcohol and water obtained a yield of 10 per cent. of the theoretical.

4-Imino-7-hydroxy-2:3-diphenyl-γ-benzopyran Hydrochloride,



This was prepared by passing a slow current of dry hydrogen chloride into a well-cooled solution of 3 grams of resorcinol and 5 grams of benzoylphenylacetonitrile in 5 c.c. of glacial acetic acid for five to six hours. The pink-coloured needles which separated were collected after three days, washed with ether, and kept on porous earthenware in a vacuum over potassium hydroxide. They shrink at 280° and melt at 286°:

0·1272 gave 0·3206 CO_2 and 0·0583 H_2O. C = 68·73; H = 5·09.
$C_{21}H_{15}O_2N,HCl,H_2O$ requires C = 68·66; H = 4·95 per cent.

The compound gives a yellowish-brown coloration with alcoholic ferric chloride.

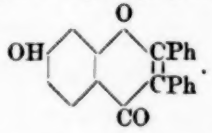
The *base* crystallised from alcohol in yellow needles melting at 290°:

0·1206 gave 0·3546 CO_2 and 0·0500 H_2O. C = 80·19; H = 4·60.
0·2164 „ 8·5 c.c. N_2 at 20° and 760 mm. N = 4·49.
$C_{21}H_{15}O_2N$ requires C = 80·50; H = 4·60; N = 4·47 per cent.

The *acetyl* derivative crystallises from alcohol in colourless needles melting at 215°:

0·1064 gave 0·2951 CO_2 and 0·0458 H_2O. C = 75·62; H = 4·78.
0·2280 „ 8 c.c. N_2 at 20° and 758 mm. N = 4·00.
$C_{23}H_{17}O_3N,\frac{1}{2}H_2O$ requires C = 75·82; H = 4·94; N = 3·83 per cent.

7-Hydroxy-2:3-diphenyl-γ-benzopyrone,



This was prepared by boiling 3 grams of 4-imino-7-hydroxy-2:3-diphenyl-γ-benzopyran hydrochloride with 30 c.c. of 10 per cent. sulphuric acid for two hours. The product separated from alcohol in colourless needles melting at 288°:

0·1112 gave 0·3262 CO_2 and 0·0458 H_2O. C = 80·00; H = 4·57.
$C_{21}H_{14}O_3$ requires C = 80·25; H = 4·45 per cent.

The *acetyl* derivative crystallises from acetic acid in colourless leaflets melting at 222°:

0·1142 gave 0·3096 CO_2 and 0·0490 H_2O. C = 73·93; H = 4·76.
$C_{23}H_{16}O_4,H_2O$ requires C = 73·80; H = 4·81 per cent.

Decomposition with Potassium Hydroxide.

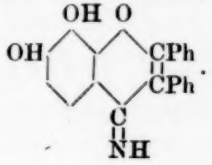
In order to prove the constitution, 3 grams of 7-hydroxy-2:3-diphenyl-γ-benzopyrone were boiled with a solution of 15 grams of potassium hydroxide in 30 c.c. of water for four hours. The solution after dilution was extracted with ether, which on evaporation gave deoxybenzoin.

The alkaline solution from which the ketone had been removed was acidified with dilute sulphuric acid and the precipitate collected. The acid solution, on extraction with ether, furnished resorcinol.

The precipitate obtained after acidification of the alkaline solution was dissolved in aqueous sodium hydroxide, and a current of carbon dioxide was passed through in order to liberate any unchanged original material. The clear solution was acidified and

extracted with ether, which on evaporation gave a mixture of a solid and an oil, the latter being eliminated by treatment with ammonia, in which it was insoluble. The ammoniacal solution on acidification gave a solid, which crystallised from hot water in colourless needles, melting at 204° (the melting point of β-resorcylic acid is 204—206°).

4-Imino-7:8-hydroxy-2:3-diphenyl-γ-benzopyran,



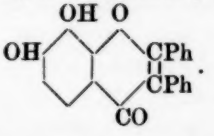
This was prepared from 3 grams of pyrogallol and 5 grams of benzoylphenylacetonitrile. After five days water was added, and the precipitate dissolved in alcohol and treated with aqueous sodium acetate. It then crystallised from dilute alcohol in yellow needles melting at 179—180°:

0·1200 gave 0·3285 CO_2 and 0·0510 H_2O. C=74·65; H=4·72.
0·1564 „ 5·8 c.c. N_2 at 17° and 764 mm. N=4·30.

$C_{21}H_{15}O_3N,\frac{1}{2}H_2O$ requires C=74·55; H=4·73; N=4·14 per cent.

The compound gave a green colour with alcoholic ferric chloride, and dissolves on warming in aqueous sodium hydroxide to a yellow solution, with the evolution of ammonia.

7:8-Dihydroxy-2:3-diphenyl-γ-benzopyrone,



This substance, prepared in the usual way from the imino-compound, crystallised from alcohol in colourless needles melting at 185°:

0·1245 gave 0·3470 CO_2 and 0·0478 H_2O. C=76·01; H=4·26.
$C_{21}H_{14}O_6$ requires C=76·36; H=4·24 per cent.

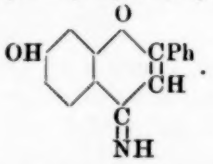
The compound is soluble in alcohol, acetic acid, or benzene, but insoluble in light petroleum or water. It gives a green colour with alcoholic ferric chloride, and reduces ammoniacal silver nitrate solution on warming. It does not fluoresce with concentrated sulphuric acid.

Attempted Condensation of Resorcinol and Benzoylphenylacetonitrile.

A mixture of benzoylphenylacetonitrile (3 grams), resorcinol (2 grams), and concentrated sulphuric acid (10 c.c.), after being kept overnight, was poured on ice. The product crystallised from alcohol in colourless needles, melting at 177—178° (the melting point of benzoylphenylacetamide is 177—178°; Walther and Schickler, *loc. cit*). (Found, C = 75·33; H = 5·43. Calc., C = 75·31; H = 5·43 per cent.)

Condensations with Benzoylacetonitrile.

4-Imino-7-hydroxy-2-phenyl-γ-benzopyran,



Concentrated sulphuric acid (15 c.c.) was slowly added to benzoylacetonitrile (3·5 grams) and resorcinol (3·5 grams), and the cooled mixture, after being kept overnight, was poured on ice. The product obtained after treating an alcoholic solution of the separated solid with aqueous sodium acetate crystallised from alcohol in yellowish-brown prisms decomposing at 185—235°:

0·1104 gave 0·2954 CO_2 and 0·0510 H_2O. C = 72·97; H = 5·13.

0·1194 „ 6·1 c.c. N_2 at 17° and 768 mm. N = 5·99.

$C_{15}H_{11}O_2N,\frac{1}{2}H_2O$ requires C = 73·17; H = 4·88; N = 5·99 per cent.

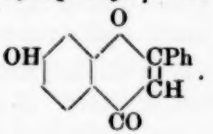
The compound is soluble in alcohol or acetic acid, sparingly so in benzene, and insoluble in light petroleum. It gives a violet coloration with alcoholic ferric chloride, and in dilute alcoholic solution shows a green fluorescence.

The *picrate* separated in bright, orange needles, melting at 238°:

0·1138 gave 12 c.c. N_2 at 17° and 760 mm. N = 12·33.

$C_{15}H_{11}O_2N,C_6H_3O_7N_3$ requires N = 12·01 per cent.

7-Hydroxy-2-phenyl-γ-benzopyrone,



Three grams of the above imino-pyran were boiled under reflux with an excess of 5 per cent. sodium hydroxide solution until no

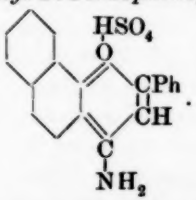
more ammonia was evolved. The solution was acidified with dilute sulphuric acid, and the product crystallised from alcohol in colourless needles, melting at 243° (Emilewicz and Kostanecki, *Ber.*, 1898, **31**, 703, give 240°).

Decomposition with Potassium Hydroxide.

In order to prove the constitution, 4 grams of 4-imino-7-hydroxy-2-phenyl-γ-benzopyran were boiled with a solution of 18 grams of potassium hydroxide in 35 c.c. of water for three hours. The solution was extracted with ether, and on evaporation of the ethereal solution an oil was obtained which was identified as acetophenone.

The alkaline solution was treated in the same way as described in the case of the decomposition of 7-hydroxy-2:3-diphenyl-γ-benzopyrone. The products obtained from the solution were resorcinol and β-resorcylic acid.

4-Imino-2-phenyl-1:4-α-naphthapyran Sulphate,



This was prepared from benzoylacetonitrile (4 grams), α-naphthol (4 grams), and concentrated sulphuric acid (20 c.c.). The product, separated by partly neutralising the clear acid solution obtained by pouring the mixture on ice, crystallised from alcohol containing dilute sulphuric acid in prisms which decomposed at 185—215°. The yield was small:

0·1100 gave 0·2486 CO_2 and 0·0386 H_2O. C = 61·63; H = 3·89.
0·2460 „ 8 c.c. N_2 at 16° and 762 mm. N = 3·80.

$C_{19}H_{13}ON,H_2SO_4$ requires C = 61·78; H = 4·06; N = 3·80 per cent.

The *base* crystallised from alcohol in pale brown prisms, decomposing at 138—148°:

0·1093 gave 0·3152 CO_2 and 0·0505 H_2O. C = 78·65; H = 5·12.
0·1047 „ 4·8 c.c. N_2 at 20° and 764 mm. N = 5·27.

$C_{19}H_{13}ON$ requires C = 78·89; H = 4·80; N = 5·17 per cent.

The *picrate* formed orange needles melting and decomposing at 274°:

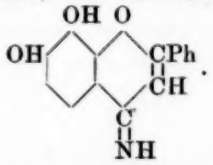
0·1230 gave 12·2 c.c. N_2 at 17° and 764 mm. N = 11·50.

$C_{19}H_{13}ON,C_6H_3O_7N_3$ requires N = 11·20 per cent.

Treatment with Dilute Sodium Hydroxide.

Three grams of the above imino-compound were boiled with 30 c.c. of 5 per cent. sodium hydroxide solution until the evolution of ammonia ceased. The solution was then acidified, when a solid mixed with some resinous material separated. This product, after repeated crystallisations from dilute alcohol, separated in colourless needles, melting at 153° (the melting point of 2-phenyl-1:4-α-naphthapyrone is 154—156°; Kostanecki, *Ber.*, 1898, **31**, 707). The yield was very small.

4-Imino-7:8-dihydroxy-2-phenyl-γ-benzopyran,



This was prepared from 4 grams of benzoylacetonitrile, 4 grams of pyrogallol, and 20 c.c. of concentrated sulphuric acid. The alcoholic solution of the viscous product obtained on pouring the acid mixture on ice was treated with an excess of aqueous sodium acetate; the substance which separated crystallised from alcohol in brown prisms decomposing at 145—165°:

0·1064 gave 0·2596 CO_2 and 0·0428 H_2O. C = 66·54; H = 4·57.
$C_{15}H_{11}O_3N,H_2O$ requires C = 66·42; H = 4·79 per cent.

The compound gives a red solution with aqueous sodium hydroxide, develops a green colour with alcoholic ferric chloride, and reduces ammoniacal silver nitrate solution on warming.

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X.—*Molecular Volumes of the Hyponitrites of the Alkali Metals and Metals of the Alkaline Earths.*

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ONE of us has already determined the molecular volumes of the nitrites of the alkali metals and metals of the alkaline earths, and has shown that certain interesting relationships obtain among them (T., 1908, **93**, 997; 1909, **95**, 66). It seemed desirable to

extend the investigation to the case of the corresponding hyponitrites, the more so as some of the physical properties of the latter have already been studied by us (T., 1913, **103**, 1562). The present paper deals with the hyponitrites of the following metals: sodium, silver, mercurous mercury and calcium, strontium, and barium. The first three metals form one group, since mercurous mercury and silver produce analogous salts, and can replace one another isomorphously (T., 1907, **91**, 2033; see also *Chem. News*, 1914, **104**, 85).

Experimental.

Sodium hyponitrite was prepared according to the modified method of Divers (T., 1899, **75**, 97; 1913, **103**, 1562). Silver and mercurous hyponitrites (Thum, *Inaug. Diss.*, Prag, 1893) were obtained by the double decomposition of sodium hyponitrite with silver nitrate and mercurous nitrate respectively. Both these salts may also be prepared from the hyponitrites of the alkaline-earth metals. The preparation of silver hyponitrite is based on the estimation of hyponitrous acid in them (Kirschner, *Zeitsch. anorg. Chem.*, 1898, **16**, 427). In order to obtain a purer salt reprecipitation of silver hyponitrite (T., 1899, **75**, 104) is advisable. The preparation of mercurous hyponitrite is described below.

Crystals of basic mercurous nitrate were triturated with water containing dilute nitric acid. The solution of mercurous nitrate, obtained in this way, was set aside, and the free mercury was allowed to settle. The hyponitrite of the alkaline-earth metal was dissolved in the minimum amount of ice-cold, nearly decinormal solution of acetic acid. The solution was next filtered, and to it mercurous nitrate was added gradually with a pipette until no further precipitate was formed. Mercurous hyponitrite dissolves in the mercurous nitrate solution, and the latter, when largely diluted, gives a yellow precipitate of a basic salt, owing to the diminution of the concentration of hydrion. In no case, therefore, should an excess of mercurous nitrate solution be added. As long as there is hyponitrous acid present in the acidified solution mercurous hyponitrite only will be precipitated, and when no excess of mercurous nitrate solution has been added, the precipitated salt may be safely washed by decantation without fear of any contamination with impurities. The neutralisation of the acid is not necessary, as mercurous hyponitrite does not dissolve appreciably in decinormal acetic acid. The precipitate, after being washed with water, was dried in a vacuum, and on analysis was found to be pure. The above precautions were also taken in the preparation of silver hyponitrite from pure sodium hyponitrite.

The preparation of calcium, strontium, and barium hyponitrites was carried out also by the double decomposition of sodium hyponitrite with the chlorides of calcium, strontium, and barium respectively. These salts are sparingly soluble in water, and are thus precipitated from the solution. When the double decomposition was carried out at the laboratory temperature (which ranges from 25° to 35° in Calcutta) the salts obtained were found to be mixtures of amorphous and crystalline varieties and to contain a variable, but always less than the required, amount of water of crystallisation. The reaction when carried out at 5° gave a salt wholly composed of crystals and containing a definite amount of water of crystallisation. The estimation of water was effected according to Kirschner's method (*loc. cit.*), and our results agree with those given by him. Calcium and barium hyponitrites contain four molecules of water of crystallisation, whilst the strontium salt contains five.

Divers had previously employed the method of double decomposition in the preparation of calcium and barium hyponitrites (T., 1899, **75**, 117). He was evidently not able to prepare barium hyponitrite containing its usual amount of water of crystallisation, since he described it as exceedingly efflorescent (see below).

In order to prepare calcium, strontium, or barium hyponitrite, a solution of the chloride of the respective metal was cooled to nearly 5°, and to it was added a solution of sodium hyponitrite cooled to the same extent. The precipitate formed was first washed with ice-cold water until free from chloride, and then again with alcohol and ether. On shaking it on paper, the product was obtained dry.

Dehydration of Calcium, Strontium, and Barium Hyponitrites.

Calcium hyponitrite does not lose its water of crystallisation over sulphuric acid (Kirschner, *loc. cit.*). Considering the possibility of dehydrating it in a vacuum, the salt was kept in it over sulphuric acid and also over phosphoric oxide for several days. The weight diminished from day to day as the salt gradually lost its water; but this diminution of weight never came to a halt. The method had, therefore, to be abandoned. It was observed that a sample of the crystalline salt in a stoppered tube had been transformed in a mass appearing like flakes of snow. On examination the substance was found to be moist, and appeared amorphous when seen under a microscope; on keeping in a vacuum it became dehydrated.

In order to ascertain the cause of this change several preparations were made, and they were daily examined with a microscope.

It was noticed that a few days elapsed before the transformation, which was gradual, had begun. The time required for the complete transformation, and that which elapsed before the change had set in, varied in the different preparations. The presence of traces of chloride was detected in all the transformed salts, and it was also noticed that a sample of the salt which had been frequently exposed to the air had absorbed a greater amount of moisture and had changed into the amorphous variety much more quickly than a sample of the same preparation that had not been so exposed. The transformation was, therefore, suspected to be due to calcium chloride and moisture combined. In order to test this further, a fresh sample of calcium hyponitrite was prepared, freed from chloride as explained above, and washed with alcohol and ether. A portion of this salt was placed in a funnel, and to it were added some drops of calcium chloride solution, the excess of which was washed away with alcohol and ether. A portion of this salt, and also some of the original salt freed from chloride, were placed over sulphuric acid in the same desiccator. Samples of both were also kept in two separate stoppered tubes. The salt mixed with chloride in the stoppered tube soon changed into the amorphous variety, whilst that kept over sulphuric acid did not undergo any such change. It is probable that calcium chloride forms with moisture a solution, which is able to enter into the interior of crystals and thus to cause the disintegration of the crystal structure (see below). The traces of chloride from the transformed salt were now removed by washing with ice-cold water and then with alcohol and water. The salt was thus obtained pure, and it became anhydrous on keeping in a vacuum:

0·1195 gave 0·1628 $CaSO_4$. Ca = 40·10.
0·1516 „ 0·3271 Ag. $H_2N_2O_2$ = 62·00.
$Ca(NO)_2$ requires Ca = 40·05; $H_2N_2O_2$ = 61·95 per cent.

Anhydrous strontium and barium hyponitrites were also prepared in the same way. The analysis of the former is given below; barium hyponitrite has already been analysed by Zorn (*Ber.*, 1882, **15**, 1008), and our analyses agree with his:

0·1216 gave 0·1514 $SrSO_4$. Sr = 59·38.
0·1640 „ 0·2396 Ag. $H_2N_2O_2$ = 42·00.
$Sr(NO)_2$ requires Sr = 59·32; $H_2N_2O_2$ = 41·99 per cent.

The crystalline salts can also be made to change into the amorphous powders readily when they are washed, first with a concentrated solution of calcium chloride, and then with alcohol and ether. The chloride present in them may be removed in the way stated before. Barium hyponitrite, moistened with xylene and

kept in a vacuum desiccator, was also noticed to fall to powder. On removing the xylene with alcohol and ether, the hyponitrite was obtained anhydrous.

The nitrogen in the anhydrous salts can be estimated by Dumas' method provided precautions are taken not to heat them even slightly before the complete expulsion of the air by carbon dioxide. (Found, N = 28·15. $Ca(NO)_2$ requires N = 28·00 per cent. Found, N = 19·05. $Sr(NO)_2$ requires N = 18·97 per cent. Found, N = 14·24. $Ba(NO)_2$ requires N = 14·19 per cent.)

Determination of Densities.

Densities of the hyponitrites have been determined at the laboratory temperature with a pyknometer in xylene with respect to the density of water at 4°. The air in the interstices of the salt was removed by placing the pyknometer, together with the salt and xylene, in a vacuum. In the following table the densities and molecular volumes of sodium, silver, and mercurous mercury are given:

Salt.	Density.	Mean density.	Mol. vol. = Mol. wt. / Density.
$Na_2N_2O_2$	2·468 2·464 2·466	2·466	42·98
$Ag_2N_2O_2$	5·78 5·75 5·72	5·75	47·96
$Hg_2N_2O_2$	7·33 7·35 7·32	7·33	62·76

The molecular volumes of nitrates and nitrites have been compared by one of us (*loc. cit.*). The relation between them and the molecular volumes of the corresponding hyponitrites is shown in the table below. In the case of the nitrates and nitrites, twice their molecular volumes (which have been calculated from their densities compared with water at 4°) have been taken for comparison with those of the corresponding hyponitrites.

Metal.	Mol. vol. of nitrate, $(RNO_3)_2$.	Difference in mol. vol. between nitrate and nitrite.	Mol. vol. of nitrite, $(RNO_2)_2$.	Difference in mol. vol. between nitrite and hyponitrite.	Mol. vol of hyponitrite, $(RNO)_2$.
Sodium	75·06	11·18	63·88	20·90	42·98
Silver	78·14	8·94	69·20	21·24	47·96
Mercurous mercury	—	—	82·96	20·20	62·76

The difference in the molecular volumes of the nitrites and hyponitrites is much greater than that in the molecular volumes

of the corresponding nitrate and nitrite. In both cases the difference in the molecular weight is due to a molecule of oxygen. The large difference between the molecular volume of the nitrites and hyponitrites is therefore to be accounted for by the diazo-constitution of hyponitrous acid as suggested by Hantzsch (*Annalen*, 1898, **299**, 68), and finally confirmed by others. The differences in the molecular volumes of the nitrates and nitrites (*loc. cit.*), as well as that of the nitrites and hyponitrites, are almost constant. The mean of the differences is 10·2 in the former case and 20·8 in the latter for a difference of O_2. When the molecular volume of one of them for a particular metal is known, that of the other two may be obtained by calculation, and from their molecular volumes their respective densities may be determined. The density of anhydrous mercurous nitrate does not seem to have been determined. The value calculated from the data of the molecular volume is 5·6.

The process of dehydration of the hyponitrites of calcium, strontium, and barium has already been described. In the following table the densities and molecular volumes of their anhydrous forms are given.

Salt.	Density.	Mean density.	Mol. vol. = $\frac{\text{Mol. wt.}}{\text{Density.}}$
CaN_2O_2	2·528 2·529 2·524	2·527	39·61
SrN_2O_2	2·683 2·689 2·683	2·683	55·05
BaN_2O_2	3·894 3·888 3·892	3·891	50·75

The element strontium has a molecular volume intermediate between those of calcium and barium. In their compounds also the molecular volumes are found to increase regularly from calcium to strontium and then to barium. It will be noticed that strontium hyponitrite has a value higher than that of calcium and barium. This is abnormal (see below).

The molecular volumes of the nitrate, nitrite, and the hyponitrite of these three metals are as follows:

	Nitrite, $R(NO_3)_2$.	Difference between nitrate and nitrite.	Nitrite, $R(NO_2)_2$.	Difference between nitrite and hyponitrite.	Hyponitrite, $R(NO)_2$.
Calcium ...	69·54	11·95	57·59	17·98	39·61
Strontium	72·24	9·58	62·66	7·61	55·05
Barium ...	80·58	9·56	71·02	20·27	50·75

The difference between the nitrite and hyponitrite is of the same order as observed in the case of sodium, silver, and mercurous mercury. The abnormality in the case of strontium is due to the unusual molecular volume of strontium hyponitrite. The constitutional formula of the hyponitrite of the univalent metals is R·O·N:N·O·R, whilst in the case of a bivalent metal it is $R<\begin{matrix}O\cdot N\\ \|\\ O\cdot N\end{matrix}$. It will be noticed that in the case of a bivalent metal a ring has been formed. In organic compounds such rings are usually associated with a contraction (Le Bas, *Phil. Mag.*, 1914, [vi], **27**, 352). In the present instances if such contraction had occurred, the differences in the molecular volumes of the nitrite and the corresponding hyponitrite of the bivalent metal would have been much more pronounced than in the case of a univalent metal.

It has been stated before that the behaviour of strontium hyponitrite is peculiar. It has a molecular volume which is greater than that of its calcium and barium analogues, and it crystallises with five molecules of water, whilst the calcium and barium salts crystallise with only four. It has also been found that strontium hyponitrite when kept over sulphuric acid loses its water of crystallisation much more easily than does barium hyponitrite, whilst the calcium salt does not do so under similar conditions.

It would be natural to expect a correlation to exist between these marked differences in properties. The method of dehydration of the above-mentioned salts indicate that in their crystals the anhydrous hyponitrite molecules are held together by their water of crystallisation. The water molecules may be assumed to surround a molecule of the hyponitrite and to become fixed on its surface, which may be taken to be spherical. The outer surfaces of such spheres, in the case of calcium, strontium, and barium hyponitrites, have been calculated from their molecular volumes, and are as follows:

	Total surface.
CaN_2O_2	$56=14\times4$
SrN_2O_2	$70=14\times5$
BaN_2O_2	$66=14\times4+10$

In the first two cases the common factor is 14 and the other factors are 4 and 5, which correspond with the number of molecules of water of crystallisation of the hydrated varieties. As the molecules of water have been assumed to be attached to the surface of the sphere of the hyponitrite molecule, if the surface occupied by a molecule of water in the above two salts be considered to be the same, the capacity of taking up water molecules as water of

crystallisation ought to be conditioned only by the surface available. Assuming a water molecule to occupy a surface equal to 14, the water of crystallisation in calcium and strontium hyponitrites would be 4 and 5 respectively—the actual number of molecules found experimentally. In the case of the barium salt the surplus surface, after the accommodation of four molecules of water, is ten (four units less than fourteen), so that an addition of another molecule of water is not possible. The foregoing idea is, of course, not new. In order to explain the phenomenon of steric hindrance, Wegscheider (*Monatsh.*, 1895, **16**, 148) assumes that ester-formation is preceded by the addition of a molecule of alcohol and acid. He further conceives that large groups or atoms in the neighbourhood of the carboxyl in the acid molecule prevent the formation of the additive compound, as they occupy the major portion of the space round the carbon atom of the carboxyl and leave little room for the addition of an alcohol molecule, thus interfering with the formation of an ester. The comparatively weaker affinity of barium, as evidenced from the heat of formation of its salts, may be an additional cause for the inability to retain a fifth water molecule.

As regards the easy removal of water from strontium hyponitrite when kept over sulphuric acid, it may be assumed that the attraction of strontium hyponitrite for an individual water molecule is less than that of the other two for the same, for in the case of the strontium salt it is distributed over five molecules of water, whilst in the case of the calcium and barium salts it is distributed over four.

In order to obtain the molecular volume of the water of crystallisation of the above salts, their densities and molecular volumes have been determined, and they are recorded below.

Salt.	Density.	Mean density.	Mol. vol. = Mol. wt. / Density.
$Ca(NO)_2,4H_2O$.....	1·834 1·836 1·832	1·834	93·83
$Sr(NO)_2,5H_2O$	2·172 2·172 2·174	2·173	109·3
$Ba(NO)_2,4H_2O$ ...	2·740 2·745 2·741	2·742	98·26

On subtracting the molecular volume of the anhydrous salt from that of the hydrated one we get the total volume occupied by water

molecules, which being divided by the number of molecules gives the molecular volume of water of crystallisation These values have been calculated as follows:

$Ca(NO)_2,4H_2O$ ..... 93·83 (mol. vol.)
$Ca(NO)_2$ ..... 39·61 ,,

Vol. of water = 54·25 ÷ 4 = 13·56 (mol. vol. of water of crystallisation).

$Sr(NO)_2,5H_2O$ ..... 109·3 (mol. vol.)
$Sr(NO)_2$..... 55·05 ,,

Vol. of water = 54·25 ÷ 5 = 10·85 (mol. vol. of water of crystallisation).

$Ba(NO)_2,4H_2O$ ..... 98·26 (mol. vol.)
$Ba(NO)_2$ ..... 50·75 ,,

Vol. of water = 47·51 ÷ 4 = 11·88 (mol. vol. of water of crystallisation).

It is very striking that the volume occupied by four molecules of water in the calcium salt is equal to that occupied by five molecules in the strontium salt. The values of the molecular volumes of water, calculated from those above, however, do not agree with the results obtained by Thorpe in the case of certain sulphates (T., 1880, **37**, 102). According to him, the differences between the monohydrate and the dihydrate is 13·3, between the dihydrate and the trihydrate 14·5, between the trihydrate and the tetrahydrate 15·4, and between the hexahydrate and the heptahydrate 16·2. The first molecule of water, which he calls the constitutional water, occupies a volume equal to 10·7. These observations are in harmony with those recorded by Kopp. Strontium hyponitrite is a pentahydrated salt, and according to Thorpe the average molecular volume of its water of crystallisation ought to be greater than the values determined from calcium and barium hyponitrites, which are tetrahydrated. Moreover, Thorpe observes that the stability of a compound is connected with the degree of contraction of the water molecules, so that when the molecular volumes of the water of crystallisation become smaller, the substance becomes more stable. It has been observed that calcium hyponitrite does not lose its water of crystallisation over sulphuric acid, whilst the strontium and barium salts do so, although the average molecular volume of water obtained in the case of the calcium salt is greater than that calculated from the strontium and barium salts. One of us has further observed that in the case of the monohydrated salt the molecular volume of water of crystallisation may be as low as 6·97 (*loc. cit.*). The work of Laue and Bragg on the structure of

crystals by means of *X*-rays has demonstrated that there are intervening spaces between atoms and molecules; that a discrepancy would arise from neglecting these spaces is thus evident.

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XI.—*Nitromercaptides and their Reaction with the Alkyl Iodides. Compounds of the Disulphonium Series.*

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THE reactivity of the mercaptans towards the mercury haloids is well known. Ethyl mercaptan, for instance, readily acts on mercuric chloride and iodide, giving rise to the formation of the compounds EtS·HgCl and EtS·HgI, which may be termed chloro- and iodo-mercaptide respectively. In the course of previous investigations the close analogy which obtains between mercuric chloride and mercuric nitrite has often been pointed out (T., 1912, **101**, 965). So close is this analogy that when a compound of mercuric chloride with an alkylamine is obtained a corresponding one with mercuric nitrite can almost be predicted (T., 1913, **103**, 3). The explanation lies in the fact that both these salts are very feebly ionised in aqueous solutions. Recently it occurred to the author that mercuric nitrite when treated with the mercaptans might yield a series of nitromercaptides. The expectation has been realised, but the phenomenal reactivity of mercuric nitrite with regard to the mercaptans results, not only in the formation of nitromercaptides of the type R·S·$HgNO_2$ (R=alkyl), but also of compounds of the type R·S·$HgNO_2$,$Hg(NO_2)_2$, that is, both substitutive and additive products (P., 1914, **30**, 140), and often mixtures of both in varying proportions. The subject has recently been more thoroughly and systematically investigated, with the result that, not only has the new and interesting series of the expected organic nitrites been isolated in a state of purity, but additional light has been thrown on their constitution by their behaviour towards the alkyl iodides.

Although from their mode of formation, described in detail below, there is scarcely any room for doubt that these mercaptides conform to the constitutional formula R·S·$HgNO_2$, it was thought

desirable further to settle this question by acting on them with the alkyl iodides; ethyl nitromercaptide, for instance, would be expected to act on, say, ethyl iodide in the following manner:

$$2EtS\cdot HgNO_2 + 2EtI = Et_2S_2 + Hg_2I_2 + 2EtNO_2,$$

the products being ethyl disulphide, mercurous iodide, and nitroethane. This is what actually happens, only in place of mercurous iodide, mercuric iodide is formed, the extra atom of iodine being derived from the ethyl iodide itself, which might decompose under favourable conditions. The most notable feature of the reaction, however, is that the ethyl disulphide, at the moment of its formation, combines with a molecule of mercuric iodide and another of ethyl iodide, which is always added in excess, to form an additive compound of the empirical formula, Et_2S_2,HgI_2,EtI, in the shape of glistening, yellow tablets. Simultaneously, at least two more compounds are formed, consisting of the above components, but evidently in different proportions, but it is not an easy task to isolate the latter in a state of purity. Methyl mercaptide also behaves similarly, and the various other alkyl iodides may also be substituted for ethyl iodide, the reaction being of general applicability, salts of the type $R_2S_2,HgI_2,R'I$ being invariably formed, where R and R′ represent different alkyl radicles.

At first sight these compounds appear to be simply "molecular" and of an additive character, but in reality they are derivatives of the sulphonium series with two sulphur atoms in the chain. Smiles has shown that mercuric iodide dissolves readily in contact with alkyl sulphides, generating well-defined salts of the empirical formula $RR'S,HgI_2$, and he suggests that these are to be regarded as sulphonium mercuric iodides. In the presence of mercuric iodide the bivalent sulphur becomes quadrivalent, and he formulates these compounds as SRR′I·HgI (T., 1900, **77**, 161; 1907, **91**, 1396).

The key to the constitution of the present series of compounds is furnished by an extension of Smiles' hypothesis to the alkyl disulphides. In the presence of mercuric and alkyl iodides the two bivalent sulphur atoms of the alkyl disulphide become quadrivalent, thus favouring the formation of salts of the type

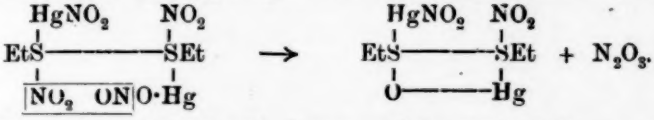
SRR′I·SRI·HgI.

The reactivity of mercuric nitrite equally favours the formation of sulphonium derivatives with one and two atoms of sulphur respectively. For instance, ethyl sulphide has been found to yield a compound of the formula $Et_2S,Hg(NO_2)_2$, which should be regarded as a sulphonium mercuric nitrite, $NO_2\cdot SEt_2\cdot HgNO_2$. When ethyl disulphide is acted on by mercuric nitrite, nitrous fumes are evolved and a white, crystalline nitrite is obtained, con-

forming to the formula $Et_2S_2,Hg(NO_2)_2,HgO$. The reaction becomes almost inexplicable if this compound is regarded simply as an additive one, as nitrous fumes may be expected to be disengaged whenever mercuric nitrite acts on a mercaptan, thus:

$$\cdot SH + Hg(NO_2)_2 = \cdot S \cdot HgNO_2 + HNO_2.$$

In the present instance there is no room for such a reaction. What evidently happens is that both the bivalent sulphur atoms become quadrivalent, thus: Et·S·S·Et, and two molecules of mercuric nitrite are now fixed, giving rise to the hypothetical compound:



As the chain is loaded with heavy radicles derived from mercuric nitrite, however, it has to part with a portion of the latter in the shape of nitrogen trioxide, generating a compound, which is at once a disulphonium salt and a cycloid. The formation of this interesting oxynitrite as suggested above, not only brings it into line with the proposed constitution of the disulphonium series of mercuric iodides, which forms the subject matter of the present communication, but may also be taken as a further confirmatory proof of this. These evidently contain one or two, as the case may be, asymmetric sulphur atoms. It should be possible to resolve them into their enantiomorphs by suitable methods. It is noteworthy that Hilditch and Smiles treated ethyl disulphide with a mixture of ethyl iodide and mercuric iodide in acetone solution and obtained a series of sulphonium iodides of entirely different formulæ—all of them being derivatives of a single sexavalent sulphur atom (*loc. cit.*).

Experimental.

Nitromercaptides.

Ethyl Nitromercaptide, $EtS \cdot HgNO_2$.—A dilute alcoholic solution of the mercaptan is added with constant stirring to a fairly concentrated solution of sodium mercuric nitrite, care being taken that the latter is always in excess. After an interval of a minute or two a crystalline, nacreous precipitate, with a faintly yellow tint, is obtained. During the reaction the solution becomes warm and nitrous fumes are liberated. The salt is washed and dried, preferably in a vacuum, over sulphuric acid. If the mercaptan solution is concentrated and if it is added all at once to the mercuric nitrite solution a pasty mass and sometimes a grey precipitate is the product, which on analysis is found to be a mixture of different salts. Ethyl nitromercaptide dissolves readily in hydro-

chloric acid with the evolution of nitrous fumes and the garlic-like odour of mercaptans. It is almost insoluble in water; 20 c.c. of water at 31° dissolving 0·0016 gram and a conductivity determination gave the following numbers:

u.	*v.*
130·5	4873
132·7	9746

The results are not very trustworthy, but they indicate that there are only two ions present:

0·1946 gave 0·0522 CO_2 and 0·0314 H_2O. C = 7·32; H = 1·79.
0·0823 „ 3·6 c.c. N_2 at 28° and 760 mm. N = 4·78.
0·1680 „ 0·1265 HgS. Hg = 64·91.
$C_2H_5O_2NSHg$ requires C = 7·82; H = 1·63; N = 4·56; Hg = 65·15 per cent.

Methyl Nitromercaptide, $MeS{\cdot}HgNO_2$.—The method of preparation is exactly the same as in the preceding case. There is much less tendency towards the formation of the pasty mass. The salt is obtained as a white, crystalline product:

0·1560 gave 7·0 c.c. N_2 at 33° and 760 mm. N = 4·79.
0·3400 „ 0·2660 HgS. Hg = 67·44.
CH_3O_2NSHg requires N = 4·78; Hg = 68·25 per cent.

Direct estimation of sulphur in the above compounds involves great difficulties. Fusion with potassium nitrate and sodium carbonate invariably gives low results. Thus in the case of ethyl nitromercaptide the percentage of sulphur was found to be 7·25, that required by theory being 10·43.

Interaction of the Nitromercaptides and the Alkyl Iodides.

Ethyl Nitromercaptide and Ethyl Iodide: Formation of the Compound Et_2S_2,HgI_2,EtI.—The nitromercaptide is shaken with an excess of the alkyl iodide, when the deep red colour of the latter, due to free iodine dissolved in it, is at once discharged. The mixture is now digested on a water-bath for two to three hours. The completion of the reaction is indicated by the formation of two distinct layers, the lower one being thick and of deeper tint and the upper one much lighter. The heavy bottom layer on cooling deposits yellow prisms and tablets. The lighter liquid is subjected to distillation. The first fraction consists almost entirely of unchanged ethyl iodide, the succeeding ones of ethyl iodide and nitroethane, and ultimately the temperature remains stationary at 113°, the boiling point of nitroethane. The isomeric ethyl nitrite is also formed, and in some experiments the amount was quantitatively estimated by the method described in a previous paper

(T., 1915, **107**, 1251). The residue in the flask consists of a dark brown liquid of the consistency of treacle. The crude, yellow crystals obtained as above are dissolved in acetone and reprecipitated by the addition of water. Care should be taken that the ether be not added in excess, for the first crop—the product of fractional precipitation—is the purest. It has been found throughout the series that at least three distinct compounds are simultaneously formed. This is particularly noticeable in the case of the interaction of methyl nitromercaptide and ethyl iodide (see below).

The *ethyldisulphoniummercuri-iodide*, Et_2S_2,HgI_2,EtI, as prepared above consists of yellow crystals melting at 112°. It is insoluble in water or alcohol, and when gently heated in a bulb tube a heavy liquid condenses in the upper stem, a sublimate of mercuric iodide is deposited, and a charred residue is left in the bulb. When it is subjected to dry distillation in a very small flask immersed in an oil-bath, at first ethyl iodide distils and later a mixture of ethyl iodide and ethyl disulphide, the temperature finally rising to 143° (the boiling point of ethyl disulphide is 151°), and a strong, disagreeable, garlic-like odour is perceptible.

Method of Analysis.—As the compounds of the present series have molecular weights ranging from 704 to 760, the percentage of carbon, which is very low, is scarcely a safe guide in assigning formulæ to them. The estimation of iodine, therefore, was considered preferable. Carius's method in the presence of mercury and halogens is quite unsatisfactory. After several failures the following method, which is a modification of that adopted for the estimation of mercury in cinnabar, was adopted and gave fairly accurate results.

The substance, contained in a porcelain boat, was placed in a tube 12 mm. in diameter and a layer of powdered copper 22 cm. in length was placed next to it, the heating being performed in a current of carbon dioxide derived from magnesite. The whole of the iodine is taken up by the copper, forming cuprous iodide. This method has the additional advantage of simultaneously yielding the mercury in the free state. The cuprous iodide when boiled with sodium hydroxide solution readily gives up its iodine and the sodium iodide in the filtrate is estimated in the usual way. Care should be taken that the weight of the substance to be analysed does not exceed 0·35 gram; otherwise the result is apt to be too low:

0·2385 gave 0·0862 CO_2 and 0·0510 H_2O. C = 9·86; H = 2·38.
0·2917 „ 0·2839 AgI „ 0·082 Hg. I = 52·51; Hg = 28·18.

$C_6H_{15}I_3S_2Hg$ requires C = 9·84; H = 2·05; I = 52·05; Hg = 27·32 per cent.

Ethyl Nitromercaptide and Methyl Iodide: Formation of the Compound, Et_2S_2,HgI_2,MeI.

A pale yellow, crystalline compound is obtained, which is further purified by dissolving in acetone and precipitating by the addition of ether. It melts sharply at 86°:

0·2710 * gave 0·2722 AgI and 0·0769 Hg. I = 54·28; Hg = 28·37.

$C_5H_{13}I_3S_2Hg$ requires I = 53·06; Hg = 27·85 per cent.

Methyl Nitromercaptide and Ethyl Iodide.

It has been already pointed out that at least three distinct compounds are simultaneously formed, and this could be well followed out in the course of the present reaction. After about three hours' digestion of the components on the water-bath, three distinct layers were recognisable, the bottom layer being viscid and of a golden-yellow colour, the middle layer rather thick and brown, and the upper layer thin and reddish-brown. The upper and middle layers were carefully decanted while still hot, whilst the bottom layer, being viscid, remained adhering to the flask. The middle portion on cooling solidified to a crystalline, brown mass. It was dissolved in acetone and shaken with ether, when a good crop of the disulphonium compound was precipitated in minute, yellow crystals. The filtrate on evaporation gave a dark brown, semi-crystalline mass of the consistency of treacle. It was redissolved in acetone and once more treated with ether, when a fine, crystalline powder was deposited and at the same time a viscid liquid separated out, which on keeping solidified to a mass of crystals; yellow, minute, oily globules were also found scattered throughout. These crystals melted at 63—65°. The filtrate from the second treatment on evaporation left a brown, slightly viscous, crystalline residue. The upper layer, which consisted chiefly of unchanged ethyl iodide, on evaporation left a few drops only of a greenish-yellow oil, the amount of which was too small for purposes of analysis. The bottom golden-yellow liquid on cooling was found to be intermixed with yellow crystals. As it was evidently a mixture no analysis was undertaken. The largest yield, however, was that of the *disulphonium* derivative, Me_2S_2,HgI,EtI, the melting point of which was 69—71°.

I. The product was simply recrystallised from acetone, but not precipitated by ether:

0·3592 gave 0·3584 AgI and 0·1097 Hg. I = 53·93; Hg = 30·54.

* The substance analysed was not purified by recrystallisation and hence the percentage of iodine is rather high.

II. In this case the substance was precipitated from acetone solution by means of ether:

0·2139 gave 0·0617 Hg. Hg = 28·85.

$C_4H_{11}I_3S_2Hg$ requires I = 54·11; Hg = 28·41 per cent.

It has almost invariably been noticed that unless the product is purified as above it is apt to be contaminated with a substance containing a higher percentage of mercury.

Analysis of the second crop (m. p. 63—65°):

0·3084 gave 0·314 AgI and 0·0918 Hg. I = 55·02; Hg = 29·77.

It will thus be evident that the second crop is slightly richer both in the percentage of mercury and of iodine, although the atomic ratio of both remains constant, namely, 1 : 3.

Ethyl Nitromercaptide and n-*Propyl Iodide: Formation of the Compound,* Et_2S_2,HgI_2,C_3H_7I.

The components after being heated as above gave a dark brown bottom layer, which yielded dark brown, shining crystals, slightly moist to the touch. These were dissolved in acetone and reprecipitated by ether. The colouring matter was thereby removed, and a pale yellow, crystalline powder was obtained. Its melting point was not very sharp, lying between 75° and 78°:

0·2744 gave 0·2596 AgI and 0·0715 Hg. I = 51·12; Hg = 26·06.

0·3080 „ 0·0836 Hg. Hg = 27·14.

$C_7H_{17}I_3S_2Hg$ requires I = 51·07; Hg = 26·81 per cent.

Methyl Nitromercaptide and n-*Propyl Iodide: Formation of the Compound,* Me_2S_2,HgI_2,C_3H_7I.

The crystalline mass obtained by treatment of the components as described above was precipitated from acetone solution by ether. In this manner yellow, mealy crystals were obtained, the melting point of which was not very sharp, being between 99° and 102°:

0·3314 gave 0·3204 AgI and 0·0912 Hg. I = 52·24; Hg = 27·52.

$C_5H_{13}I_3S_2Hg$ requires I = 53·06; Hg = 27·86 per cent.

Ethyl Disulphide and Mercuric Nitrite: Formation of the Compound, $Et_2S_2,Hg(NO_2)_2,HgO$.

On gradually adding an alcoholic solution of the disulphide to mercuric nitrite with brisk stirring nitrous fumes are disengaged and a crystalline powder is precipitated, which, under the microscope, is found to consist of needles. The salt readily dissolved in hydrochloric acid with copious liberation of nitrous fumes:

0·2178 gave 0·0552 CO_2. C = 6·91.
0·1173 „ 4·8 c.c. N_2 at 30° and 760 mm. N = 4·43.
0·1082 „ 0·0805 HgS. Hg = 64·15.
$C_4H_{10}O_5N_2S_2Hg_2$ requires C = 7·62; N = 4·45; Hg = 63·50 per cent.

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XII.—*Studies on the Oxidation of Unsaturated Fatty Oils and Unsaturated Fatty Acids. Part I. The Formation of Acrolein by the Oxidation of Linseed Oil and Linolenic Acid.*

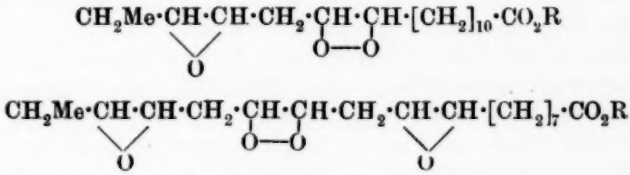
By ARTHUR HENRY SALWAY.

IT has long been known that fatty oils possessing a high degree of unsaturation undergo a profound change when exposed to the air, being gradually converted into viscid liquids or varnish-like solids. This phenomenon, commonly termed "drying," has been frequently studied with the object of determining the nature of the chemical reactions which accompany the change, but the results obtained are insufficient to enable a satisfactory formulation of the process to be made. Hence the mechanism of the change is still a matter for further investigation.

It was early recognised that the "drying" of oils is associated with the absorption of oxygen from the atmosphere, and quantitative experiments (Lippert, *Zeitsch. angew. Chem.*, 1898, **11**, 412; Weger, *Chem. Rev. Fett-Harz-Ind.*, 1899, **4**, 301; and others), in which thin films of linseed oil were exposed to air, show that the oil is able to absorb about 20 per cent. of its weight of oxygen. Kissling (*Zeitsch. angew. Chem.*, 1891, **4**, 395) has shown that sterilised linseed oil exposed to sterilised air also absorbs oxygen, thus proving that the change is not induced by the presence of micro-organisms. Exposing the oil to bright sunlight increases the rapidity of the oxygen absorption, and it has been shown by Genthe (*Zeitsch. angew. Chem.*, 1906, **19**, 2087) that linseed oil exposed to ultra-violet light is capable of absorbing as much as 34 per cent. of its weight of oxygen from the atmosphere.

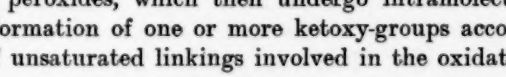
With regard to the chemical changes which are involved in the oxidation of linseed oil, it has been observed frequently that volatile products are formed and liberated during the process

(Kissling, *loc. cit.*). Noerdlinger (D.R.-P. 167137 of 1906) has shown that the volatile products contain fatty aldehydes which begin to boil at 150°, and fatty acids beginning to distil at 190°, whilst small quantities of volatile alcohols and esters are said to be present. Recent investigations by Baly (*J. Soc. Chem. Ind.*, 1912, **31**, 515), Gardner (*J. Ind. Eng. Chem.*, 1914, **6**, 91), and King (*J. Ind. Eng. Chem.*, 1915, **7**, 502), who have each examined the volatile products from oxidised linseed oil with a view to ascertain why the inhalation of vapours from linseed oil paints frequently induce symptoms of poisoning, have yielded some interesting results. Gardner and King show that carbon monoxide and carbon dioxide are evolved during the drying of linseed oil, whilst Baly states that an unsaturated aldehyde of a poisonous character is formed. The volatile products emanating from oxidised linseed oil are, however, comparatively small in amount, and by far the greater portion of the oil is converted into a non-volatile, varnish-like solid. Efforts have been made to ascertain the character of this substance, but without much success. It is evidently a mixture, and no compound of undoubted homogeneity has been isolated from it. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658) has separated it by water into a soluble and insoluble portion, which he suggests are oxidation products of linolic and linolenic glycerides respectively, possessing the following constitutions:



There is, however, no evidence that these substances are homogeneous.

Various conjectures have been made regarding the mechanism of the "drying" process. Fahrion (*Zeitsch. angew. Chem.*, 1910, **23**, 723) believes that the unsaturated compounds of linseed oil first form peroxides, which then undergo intramolecular changes with the formation of one or more ketoxy-groups according to the number of unsaturated linkings involved in the oxidation, thus:



The ketoxy-compounds are then supposed by Fahrion to undergo condensation with elimination of water, thus forming the substance known as linoxin. Fokin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276)

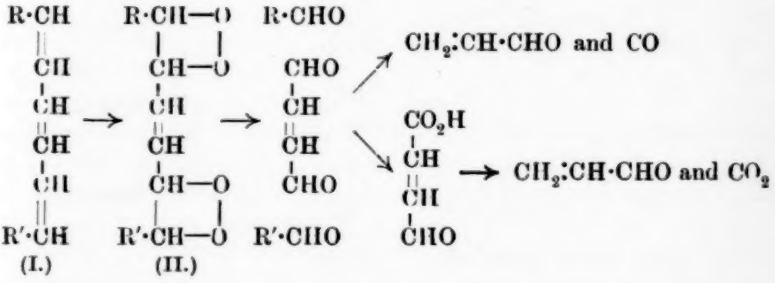
considers, on the other hand, that the primary product in the oxidation is an oxide represented by the formula $R\cdot CH\cdot CH\cdot R'$ (with O bridging the two CH groups).

Kitt (*Chem. Rev. Fett-Harz-Ind.*, 1901, **8**, 40) has endeavoured to ascertain, by acetylation of the oxidised oil, whether hydroxy-compounds are formed, but the results were inconclusive.

From the foregoing brief survey of the literature it will be seen that comparatively little is known regarding the chemical changes which linseed oil undergoes on oxidation. It is, moreover, evident that a satisfactory explanation of the process cannot be reasonably expected until the oxidation of each of the constituents of that oil is fully understood. For that reason it would be better to attempt the solution of the problem by investigating the action of air or oxygen on the glycerides of linolenic, linoleic, and oleic acids successively, but as these substances cannot readily be obtained in a pure state recourse must be had to the corresponding free fatty acids, which are more readily obtained pure (compare Erdmann, *Zeitsch. physiol. Chem.*, 1911, **74**, 179). This method of investigation of the "drying" process seems quite permissible, since it is known that the glycerol of fatty oils plays no active part in the oxidation. Accordingly, the author has undertaken an investigation of the products formed when unsaturated acids are exposed to air or oxygen. The present communication, however, deals entirely with the new observation that acrolein is one of the volatile products of oxidation of linolenic acid and of oils containing glycerides of this acid. It has previously been noticed by Dunlop and Shenk (*J. Amer. Chem. Soc.*, 1903, **25**, 826) that a sample of linseed oil gave, on drying, an odour of acrolein, and the formation of this substance was attributed to the action of oxygen on the glycerol in the oil. This view of its formation is, however, erroneous, for in the light of the results recorded below there is no doubt that the acrolein is formed directly from the fatty acids. It is here shown that when linolenic acid, or the fatty acids from linseed oil, are caused to absorb oxygen, acrolein is one of the volatile substances evolved, but no trace of this substance is produced when oleic acid is oxidised. This observation is of considerable interest in view of the light it may throw on the constitution of linolenic acid. Erdmann and his pupils (*Ber.*, 1909, **42**, 1324; *loc. cit.*) have concluded from their investigations that there are two stereoisomeric linolenic acids (compare, however, Rollett, *Zeitsch. Physiol. Chem.*, 1909, **62**, 422), each of which is represented by the constitutional formula:

$$CH_2Me\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot [CH_2]_7\cdot CO_2H.$$

It is difficult, however, to explain satisfactorily the formation of aerolein from such a compound. On the other hand, supposing linolenic acid contained the grouping R·CH:CH·CH:CH·CH:CHR′ no such difficulty would be encountered. Thus, in the first place, the linolenic acid (I) absorbs oxygen with the formation of an oxygenide (compare Salway and Kipping, T., 1909, **95**, 166), and since the central point of unsaturation should be relatively stable there would be a tendency to form the dioxygenide (II). This would then decompose, either spontaneously or in the presence of moisture, with the formation of aldehydes, including fumaraldehyde as shown below. This unknown aldehyde is unstable, and immediately suffers direct disruption with the formation of acrolein and carbon monoxide, or, on the other hand, is partly oxidised, with subsequent elimination of carbon dioxide and acrolein:



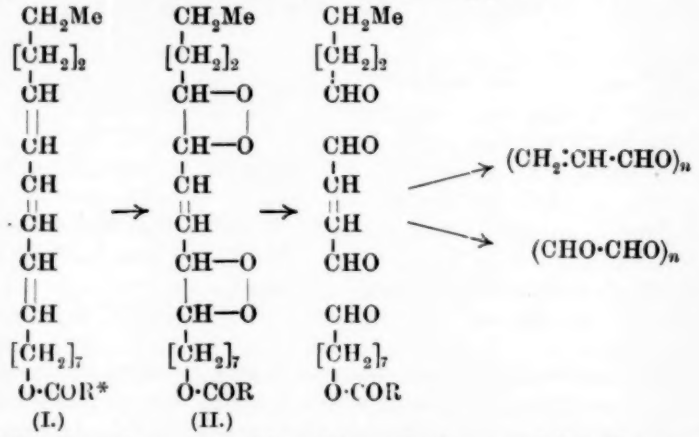
This explanation of the change not only accounts for the formation of acrolein, but also furnishes a reason for the production of carbon monoxide and carbon dioxide, as observed by Gardner and King (*loc. cit.*).

As already indicated, this view of the constitution of linolenic acid is not in agreement with the conclusions of Erdmann. The discrepancy possibly arises from the presence in linseed oil of two structurally isomeric linolenic acids, the one of which is the linolenic acid of Erdmann, whilst the other contains the unsaturated grouping suggested above. There is some support for this supposition, since it has been observed that different specimens of linolenic acid gave, under comparable conditions, varying quantities of acrolein on oxidation. It is, however, hoped that further investigation will reveal the cause of these differences.

It will be observed that linolenic acid, according to the view here given, is a derivative of hexatriene. It is known that hexatriene readily absorbs oxygen from the atmosphere, but as far as the author is aware the products of oxidation have not been closely investigated. For that reason it would be desirable to examine

hexatriene, and compounds of this type, in order to ascertain whether acrolein is formed from them by oxidation.

The formation of acrolein by the oxidation of highly unsaturated oils suggests a theory which may be advanced, with due reserve, for the explanation of the "drying" of oils. In the first place, the glyceride of linolenic acid (I) present in the oil absorbs oxygen, and the oxygenide (II) thus obtained is wholly or partly decomposed with the formation of aldehydes, including acrolein. The greater portion of the aldehydes then polymerise, and form, with the unchanged oil, the well known elastic varnish—linoxyn. From this point of view the "drying" of linolenic glyceride would be represented by the following scheme, and the dry oil would then be expected to contain polymerised acrolein and glyoxal:



Whilst there is considerable evidence in favour of this theory of the "drying" of oils, the author recognises that further research is necessary before its validity can be considered established.

Experimental.

Specimens of linseed oil which have been exposed to the atmosphere for some time always possess a strong odour, and occasionally the characteristic sharp acrolein smell can be detected. The amount of acrolein formed under these conditions is not, however, sufficient to enable it to be definitely identified. On the other hand, by conducting the oxidation at 100° in an atmosphere of oxygen, as described below, sufficient acrolein was obtained to prove its identity beyond doubt.

* For convenience, the glycerol residue is represented by R. It should also be understood that the author does not wish to commit himself with regard to the position of the hexatriene group in the chain of 18 carbon atoms.

The Formation of Acrolein by the Oxidation of Linseed Oil.

The vessel in which the oxidation was effected consisted of a large pipette bent in the shape of a U-tube, the bulbed limb of which was connected with a wash-bottle containing water, whilst the other limb was in direct communication with a manometer and an oxygen cylinder. For each experiment the pipette was about half filled with the oil and oxygen then introduced under two atmospheres' pressure, the exit tube leading to the wash-bottle being closed. The pipette was then immersed in water at 100° and vigorously shaken by a mechanical agitator with vertical motion, by means of which intimate contact of the oil and oxygen was effected. When the pressure of gas in the pipette had been reduced to one atmosphere by absorption of oxygen, the exit tube was opened and oxygen passed through the pipette. In this way the gaseous products of oxidation were made to bubble through the water contained in the wash-bottle. The pipette was then closed again and the process of oxidation and collection of volatile products repeated until the absorption of oxygen had almost ceased.

In a typical experiment with linseed oil the absorption of oxygen at the commencement of operations was very slow, but after a period of about twenty minutes the oxidation was rapid and continued so until the oil had absorbed 5 litres of oxygen per 100 grams of linseed oil. The wash water, through which the gaseous products of oxidation had been passed, had the strong and characteristic odour of acrolein; it also readily decolorised bromine water and reduced ammoniacal silver nitrate solution; it was free from acidic substances, 1 drop of $N/10$-alkali being sufficient to render the liquid alkaline. In order to identify the acrolein definitely, a quantity of the aqueous solution, obtained as described above, was shaken with freshly precipitated silver oxide until the odour of acrolein had entirely disappeared. The mixture was then filtered and the filtrate concentrated to a small bulk under diminished pressure. The concentrated solution was again filtered, to remove a small amount of silver which had separated, and then set aside to cool, when a crystalline silver salt was deposited. A further crop of crystals was obtained by the addition of alcohol to the mother liquors. The two fractions of silver salt were analysed separately with the following results:

(*a*) 0·0130 silver salt gave 0·0079 Ag. Ag = 60·8.
(b) 0·0110 „ „ „ 0·0066 Ag. Ag = 60·0.

$C_3H_3O_2Ag$ requires Ag = 60·3 per cent.
$C_3H_5O_2Ag$ „ Ag = 59·7 „ „

It is evident from these figures that the substance is either silver

acrylate or silver propionate. From other evidence, namely, the odour and the unsaturation of the original aldehyde, it is clear that the latter is acrolein, and not propaldehyde.

The Formation of Acrolein by the Oxidation of the Fatty Acids from Linseed Oil.

A quantity of linseed oil was saponified and the soap solution treated with dilute mineral acid. The liberated fatty acids were then well washed with water, dried with anhydrous sodium sulphate, and filtered. The product had an iodine value of 197·2 and was free from glycerides or glycerol. The oxidation of this substance was conducted in the manner already described in connexion with the oxidation of linseed oil. The water used for washing the gases issuing from the oxidation had the penetrating odour of acrolein, and silver acrylate was formed by agitating the solution with silver oxide. The silver acrylate was separated into two fractions by crystallisation, and then analysed. (Found, Ag = 60·1, 59·6. $C_3H_3O_2Ag$ requires Ag = 60·3 per cent.)

The amount of silver acrylate obtained from the oxidation of the fatty acids of linseed oil was greater than the amount in a corresponding experiment with linseed oil. Thus 100 grams of the fatty acids yielded 0·510 gram of silver acrylate, whilst linseed oil under the same conditions yielded 0·370 gram. There is therefore no doubt that the acrolein obtained in these oxidations is derived from the fatty acids, and not from the glycerides.*

Formation of Acrolein by the Oxidation of Linolenic Acid.

The linolenic acid employed for this oxidation had an iodine value of 269·3, and a molecular weight, as determined by titration, of 283. Fourteen grams of the acid were oxidised in the usual way at 100°, about 1 litre of oxygen being absorbed. The aqueous liquid, through which the gaseous products of oxidation were passed, had a strong odour of acrolein, and the latter was identified by conversion into silver acrylate. The amount of silver acrylate per 100 grams of linolenic acid was 0·34 gram.

Oxidation of Oleic Acid.—Thirty grams of pure oleic acid were treated with oxygen at 100° in the apparatus described above. The absorption of oxygen was relatively slow and had almost ceased when 300 c.c. had been taken up. There was no odour of acrolein in the water used for washing the volatile products, and no silver

* Pure glycerol did not yield acrolein when treated at 100° with oxygen in the manner here described.

acrylate could be isolated from it. It is thus evident that acrolein is not formed by the oxidation of oleic acid.

It would be of considerable interest to ascertain whether pure linoleic acid yields acrolein on oxidation, but there appears to be no trustworthy method of obtaining this acid in a state of purity. A specimen of Kahlbaum's linoleic acid was found to yield acrolein, but the acid had an iodine value of 195, and evidently contained linolenic acid, so that the result was inconclusive. From theoretical considerations one would not expect pure linoleic acid to yield acrolein on oxidation. There appears to be little doubt that the acrolein obtained in all these experiments is derived from linolenic acid, especially as other fatty oils known to contain this acid have been found to yield considerable quantities of acrolein on oxidation.

The author desires, in conclusion, to express his indebtedness to Lever Bros., Ltd., and Mr. J. L. Buchanan, Managing Director of the Research Department, for permission to publish the results of this investigation.

RESEARCH DEPARTMENT,
LEVER BROTHERS, Ltd.,
PORT SUNLIGHT. [*Received, December 23rd*, 1915.]

XIII.—*The Colouring Matter of Cotton Flowers. Part III.*

By ARTHUR GEORGE PERKIN.

IN a former communication it was shown (T., 1909, **95**, 2181) that the yellow flowers of the Egyptian cotton plant contain gossypitrin, a glucoside of gossypetin, and two quercetin glucosides, namely, quercimeritrin and *iso*quercitrin. The present work was undertaken to ascertain as far as possible if there was any chemical distinction not only between the Egyptian and ordinary Indian yellow cotton flower, *Gossypium herbaceum*, but also between these and the red, pink, and colourless petals of other varieties. As a side issue it was interesting to attempt to determine if the red colouring matter present in both the red and yellow flowers was due to the red oxidation products of either gossypetin or gossypitrin (T., 1913, **103**, 565).

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Owing to a failure to obtain a fresh supply of the Egyptian flowers the investigation of the first point cannot be considered

complete, the results here given, which were finished fully eighteen months ago, having been hitherto held back on this account.

The author is indebted to Mr. H. Martin Leake, Economic Botanist for the Government of the United Provinces of Agra and Oudh, for the samples of flowers, these being obtained from special varieties of the plant which he has himself investigated (*Proc. Roy. Soc.*, 1911, [*B*], **83**, 447). Among the types of cotton grown there are (*a*) red, (*b*) pink, (*c*) yellow, and (*d*) white flowered plants. In the offspring of a cross between (*a*) and (*c*) there occur in the second and subsequent generations red and yellow flowered plants, which breed pure, whereas in the offspring of a cross between (*a*) and (*d*) all four forms occur which breed pure. The petals employed in this work were derived from such pure plants, occurring among the offspring of one or other of these crosses.

The types were as follows: red flowered, *G. arboreum*, Linn.; pink, *G. sanguineum*, Harsk; yellow and white, two varieties of *G. neglectum*, Tod, usually now treated as one species, but originally described as *G. neglectum* and *G. rossrum*. With rare exception little has been done as regards the examination of flavone constituents in the flowers of plant varieties except in a haphazard manner, although mention may be made of the work of Wheldale and Bassett (*Biochem. J.*, 1913, **7**, 441; 1914, **8**, 204) on the flower pigments of *Antirrhinum majus*, in which certain varieties are shown to contain apigenin and others luteolin.

Flavones being present in general as glucosides which are colourless or nearly so, they themselves can exert little or no yellow colour effect, although such is sometimes presumed to be the case, and it would indeed appear probable that where a yellow tint is due to their agency, this is to be traced, as in the case of the yellow cotton flower, to their presence as a potassium or other salt.

That the anthocyanin of flowers is closely connected with the flavone glucoside also present was correctly surmised by Wheldale ("Report to the Evolution Committee of the Royal Society," 1909, **5**, 1), but her suggestion that the former represents an oxidation product of the latter is no longer tenable. Owing to the brilliant work of Willstätter with Everest (*Annalen*, 1913, **401**, 189) and others, the chemistry of many of these compounds is clear, and, indeed, they must now be regarded as the effect of a reduction rather than an oxidation on the flavone glucosides. As a reducing agent Everest (*Proc. Roy. Soc.*, 1914, [*B*], **88**, 603, 326) has employed magnesium turnings with alcoholic hydrochloric acid, and there can be no doubt that flavone glucosides give anthocyanins in this manner which are identical with those naturally occurring in plants.

Wheldale and Bassett again (*loc. cit.*) sought in the case of *Antirrhinum majus* to isolate the anthocyanin (anthocyanidin) from the highly-coloured flower extract by hydrolysis with sulphuric acid. In this manner they obtained magenta-red and Indian-red powders, which with dilute alkali gave green solutions. The nature of these products, which bear some resemblance to compounds described later, is uncertain, for they do not agree in their general properties with those typical of the anthocyanidins described by Willstätter and by Everest. Most probably they represent alteration products of the anthocyanidin at first produced, and into which it passes by prolonged contact with the boiling dilute mineral acid.

Experimental.

Red Cotton Flowers, G. arboreum, Linn.

The flowers (1600 grams) were extracted with boiling alcohol, the rich red-coloured extract evaporated, diluted with hot water, and the alcohol evaporated. After agitation with ether to remove wax and a trace of free colouring matter, the red liquid was boiled with lead acetate solution, which caused the separation of a greenish-brown precipitate. This was collected, washed, and, in the form of a thin cream, decomposed with hydrogen sulphide. The well-boiled mixture gave after filtration a deep maroon-coloured liquid, which when evaporated for several days in a vacuum deposited some quantity of a gelatinous mass possessing the same tint. This product (the filtrate from which is designated *A*) after being washed with a little water, was dissolved in 25 c.c. of 40 per cent. alcohol, and the red-coloured, semi-gelatinous deposit which separated on cooling, was twice recrystallised from 10 c.c. of alcohol, and finally from dilute alcohol. The product (3 grams) consisted of small, pink needles, the red-coloured impurity remaining chiefly in the mother liquors which were added to the filtrate *A*, but as the last traces of this latter adhered tenaciously to the substance, for economy's sake a special process was adopted. This consisted in pouring a concentrated alcoholic solution into ether, which caused the immediate precipitation of the red substance, and this being rapidly removed the ethereal liquid was agitated with water. The aqueous liquid gradually deposited a semi-gelatinous precipitate, which on boiling with a little water became crystalline. It could be further purified by crystallisation from dilute alcohol containing a little pyridine, a trace of the pink impurity first separating out. The yield was 2·28 grams. (Found (dried at 160°), C = 53·96; H = 4·68. $C_{21}H_{20}O_{12}$ requires C = 54·31; H = 4·31 per cent.)

After crystallisation from dilute alcohol the air-dried substance

contains two molecules of water of crystallisation. (Found at 160°, $H_2O = 7{\cdot}04$. $C_{21}H_{20}O_{12},2H_2O$ requires $H_2O = 7{\cdot}22$ per cent.)

By hydrolysis with 1 per cent. boiling dilute sulphuric acid, the glucoside gave 64·8 per cent. of a yellow, crystalline product, the analysis and general properties of which coincided with those of quercetin. (Found, $C = 59{\cdot}59$; $H = 3{\cdot}36$. $C_{15}H_{10}O_7$ requires $C = 59{\cdot}60$; $H = 3{\cdot}30$ per cent.) The acetyl compound melted at 194—196°.

The sugar present in the acid filtrate from the quercetin was isolated in the usual manner, and proved to be dextrose, in that it gave the osazone melting at 204—205°.

The hydrolysis of the glucoside thus proceeds according to the following equation:

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6,$$

which involves a yield of 65·09 per cent. of quercetin. Dyeing experiments employing mordanted woollen cloth and other comparative tests proved that this glucoside is identical with the *iso*quercitrin which, together with quercimeritrin and gossypitrin, is present in the yellow Egyptian cotton flowers.

The red aqueous filtrate *A* on evaporation in a vacuum gave a further deposit of *iso*quercitrin, and by careful examination the presence of a second flavone glucoside could not be detected in these flowers.

A sharp chemical distinction between these red cotton flowers and the yellow Egyptian flowers previously examined is thus obvious.

The final mother liquor from the *iso*quercitrin had a deep red colour and when highly concentrated in a vacuum deposited a red, viscous substance, which could not be isolated in a crystalline condition. In solution its colour, although slightly duller, was very similar to that of the original alcoholic extract, which thus apparently possessed considerable stability. That it could scarcely represent a phobaphen or partly decomposed tannin glucoside seemed certain, because although some cotton flowers, especially those which are yellow, do contain much phlobotannin, this is present in the form of a potassium or other salt, and is insoluble in alcohol. It has been previously shown that gossypetin is readily oxidised to the dull red quinone, gossypitone, this change taking place very readily even during the dyeing operation. In the case of the cotton flowers it thus appeared possible that the red coloration might not be due in this case to a typical anthocyanin, but rather to the oxidation product of the gossypetin glucoside. To determine this point, the red, viscous residue was submitted to the action of boiling 1 per cent. sulphuric acid solution, causing the

separation of a resinous precipitate. This was collected and dried, and in order to remove quercetin, which was present in some quantity, it was dissolved in pyridine and precipitated from this solution by means of ether, this operation being twice repeated. For analysis it was dried at 160° for a long period. (Found, C = 55·92; H = 4·58.) It consisted of a dull red powder, very similar to gossypitone, with which also the analytical numbers show some slight agreement. Again, with aluminium mordanted calico it dyed, although not very readily, an olive shade, resembling that given by the latter substance. On the other hand, whereas sodium hydrogen sulphite solution rapidly converts gossypitone into gossypetin, the boiling red-coloured solution of this product on addition of the reagent did not become yellow, but merely paler and somewhat browner. When neutralised with acid again, ether extracted from the liquid but a trace of flavone, which dissolved in alkali with a pure yellow colour. The evidence, therefore, of the presence of gossypitone or its glucoside in the red flowers is thus of a negative character. Dilute alkalis dissolved the product with a greenish-yellow colour, whereas sulphuric acid gave a brown solution, passing to red on dilution with water.

The Yellow Flowers, G. neglectum.

The yellow flowers (1000 grams) were extracted with alcohol and the alcoholic solution evaporated to a small bulk. On cooling, but a trace of a dark brown-coloured deposit separated, and a distinction was thus at first sight apparent between this extract and that of the yellow Egyptian flowers, which in these circumstances at once yield a heavy precipitate of the potassium salt of crude quercimeritrin. It was, however, subsequently observed that on keeping for a long period a similar separation in this case also gradually occurred. This was collected,* washed with alcohol, dissolved in hot water, and the filtered liquid treated with lead acetate, causing the formation of a dull, red-coloured precipitate, which was decomposed with hydrogen sulphide in the usual manner. The glucosidal solution on keeping for some days in a vacuum deposited a semi-gelatinous precipitate, which on recrystallisation from dilute alcohol formed warty nodules admixed with gelatinous matter. This product readily dissolved in hot water, but on boiling the concentrated solution for a few seconds the hot liquid became semi-solid owing to the separation of fine needles. These were collected, washed with warm water, and although now pure could be

* Such a separation is not really necessary, and it is simpler to add water, evaporate the alcohol, remove wax, and precipitate the aqueous liquid.

recrystallised by employing a very large volume of boiling water. (Found, C = 52·58, 52·26; H = 4·38, 4·39. $C_{21}H_{20}O_{13}$ requires C = 52·50; H = 4·17 per cent.)

When prepared in this way the glucoside is devoid of water of crystallisation, melts at 240—242°, dissolves in alkalis with a pale yellow colour, and gives with lead acetate a deep red precipitate. It is sparingly soluble in boiling alcohol, and almost insoluble in boiling acetone, a property which readily distinguishes it from quercimeritrin, which is fairly soluble in the latter solvent.

When crystallised from acetic acid and water the air-dried product contains two molecules of water of crystallisation, which it loses at 160° but regains on keeping in moist air. (Found, H_2O = 7·02. $C_{21}H_{20}O_{13},2H_2O$ requires H_2O = 6·97 per cent.)

The glucoside (0·5162 gram) when suspended in boiling water was found to be somewhat stable towards the action of acid (boiling with 7 per cent. sulphuric acid for two hours), and in this respect it resembles quercimeritrin (*loc. cit.*). The yield of yellow, crystalline product (dried at 160°) thus obtained was 66·6 per cent. This possessed all the properties of gossypetin, and yielded acetyl gossypetin melting at 226—228°. From the acid filtrate, the sugar was isolated in the usual manner, and identified as dextrose by means of the osazone, which melted at 204—205°.

The hydrolysis of the glucoside occurs, therefore, according to the following equation, which requires a yield of 66·25 per cent. of gossypetin:

$$C_{21}H_{20}O_{13} + H_2O = C_{15}H_{10}O_8 + C_6H_{12}O_6.$$

The *acetyl* derivative, $C_{21}H_{11}O_{13}(C_2H_3O)_9$, is readily produced by boiling with acetic anhydride for three hours. On cautious addition of alcohol to the solution a semi-solid, crystalline mass is produced, and the product can be recrystallised from acetic anhydride and alcohol in a similar manner. (Found, C = 54·35, 54·32; H = 4·46, 4·52. $C_{39}H_{38}O_{22}$ requires C = 54·54; H = 4·43 per cent.) It consisted of colourless needles melting at 226—228°, almost insoluble in alcohol.

An acetyl determination by the acetic ether method gave: acetic acid = 62·81, and gossypetin, 37·26; the numbers required by the above formula being respectively 62·93 and 37·06 per cent. It is accordingly an ennea-acetyl derivative.

During the examination of the Egyptian flowers (*loc. cit.*) a gossypetin glucoside, $C_{21}H_{20}O_{13}$, termed gossypitrin, was isolated; this melted at 200—202°, and was obtained in small amount as the middle fraction between quercimeritrin and *iso*quercitrin. It appeared, therefore, that gossypitrin and the glucoside present in the *G. neglectum* melting at 240—242° were distinct compounds,

for it was unlikely that the former had been isolated in so impure a condition as its low melting point would indicate. No Egyptian flowers being available, the matter remained uncertain, until it was accidentally elucidated as follows: The gossypetin glucoside melting at 240—242° was digested for some time with boiling acetone to determine if quercimeritrin was present. Under this treatment the fine, hair-like needles were broken up into much finer needles, and these when collected and dried at 100° now melted at 200—202°. When dried at 160° 1 molecule of water of crystallisation was evolved, which was, however, reabsorbed at the ordinary temperature in the presence of moist air. (Found $H_2O = 3{\cdot}72$. Calc., $H_2O = 3{\cdot}61$ per cent.) Curiously enough the anhydrous substance when plunged at once into hot sulphuric acid also melted at 200—202°, so that this lower melting point does not arise from the presence of water of crystallisation. By boiling with absolute alcohol for one hour the melting point of the undissolved portion is almost the same, but if boiling water is employed crystals quickly commence to separate from the hot solution, which now melt at 239—242° and remain anhydrous after exposure to moist air. The glucoside thus exists in two interchangeable modifications, and it is accordingly certain that both Egyptian and Indian flowers contain the same substance, gossypitrin.

In the mother liquors obtained during the isolation of gossypitrin from these flowers no certain evidence of the presence of quercimeritrin, so readily obtained from the Egyptian variety, could be detected. By further evaporation in a vacuum a second gelatinous deposit separated, but this was of so readily soluble a nature that by crystallisation from dilute acetic acid and other methods but a trifling amount of an apparently pure product crystallising in yellow needles could be isolated. Although on hydrolysis these yielded quercetin, identified by means of its acetyl derivative melting at 194—196°, their ready solubility distinguished them in a marked manner from quercimeritrin. The final mother liquor, which possessed a reddish-brown colour, also contained much of a readily soluble quercetin glucoside, and is referred to later (*B*). The aqueous filtrate from the lead precipitate, on treatment now with basic lead acetate, gave some quantity of a yellow precipitate. By decomposition in the moist condition with hydrogen sulphide in the usual manner, this yielded a solution from which nodules separated on keeping. These after recrystallisation from dilute acetic acid consisted of pale yellow needles melting at 217—219°, and when hydrolysed gave quercetin. This glucocide proved to be the same *iso*quercitrin which is present in the Egyptian flowers (*loc. cit.*) and in the red petals of *G. arboreum*.

An examination of the ordinary yellow Indian cotton flower, *G. herbaceum*, available in small amount, gave the same results as those furnished by *G. neglectum*. So far, therefore, it is certain that both the Egyptian and Indian yellow flowers contain the glucosides gossypitrin and *iso*quercitrin, although curiously enough quercimeritrin, an important constituent of the former, is apparently absent, or at least present in but small amount in the latter. It is impossible, however, to decide this point unless very much larger amounts of raw material are available than was here the case.

The mother liquor (*B*), as above noted, possessed a reddish-brown colour, this tint being apparently due to the fact that at the base of these petals a red spot or eye is present, which has the same shade as that of the petals of *G. arboreum*. On digestion with boiling dilute hydrochloric acid a precipitate containing much quercetin was deposited, and from this, by the same method as that employed previously, 0·15 gram of a dull red powder was isolated. (Found, C = 59·87; H = 3·63.) In appearance and general properties it was indistinguishable from the product derived from *G. arboreum*, except that its alkaline solution possessed a somewhat stronger green tint. The analytical figures are, however, interesting in that they differ but little from those given by quercetin itself.

Experiments with the white Indian cotton flowers, *G. neglectum* or *rossrum*, showed that these were devoid of dyeing property. One kilo. when extracted with boiling alcohol gave, by the method employed in the former cases, a nearly colourless solution, from which by means of lead acetate a very small quantity of a buff-coloured precipitate separated. From the latter by decomposition with hydrogen sulphide a minute amount of glucoside in the gelatinous condition was isolated, which by hydrolysis with acid gave a trace of impure colouring matter. This, which consisted of a buff-coloured powder, in its general reactions closely resembled apigenin, and with little doubt consisted of this or a very similar compound. The pink flowers, *G. sanguineum*, gave also a disappointing result. Employing aluminium mordanted calico a faint green shade was produced, whereas the mere trace of flavone which could be isolated from them, although probably quercetin, could not be identified with certainty.

The Oxidation Product of Gossypitrin.

It was previously pointed out that whereas gossypetin by means of alcoholic *p*-benzoquinone gives the quinone gossypitone, the glucoside gossypitrin yields also an apparently similar compound, which could not then be studied owing to lack of material. When a cold saturated solution of gossypitrin in absolute alcohol is treated

with an alcoholic solution of *p*-benzoquinone, the yellow liquid quickly becomes maroon-coloured and on gentle warming needles commence to separate. These were collected and washed with alcohol. (Found, C = 52·52; H = 3·76. $C_{21}H_{18}O_{13}$ requires C = 52·72; H = 3·76 per cent.)

This compound, for which the name *gossypitrone* is suggested, consists of maroon-coloured needles, which, however, possess a more violet tint when during their preparation dilute alcohol is employed. When heated, it gradually decomposes above 200° and does not possess a definite melting point, although fusion of the product occurs at about 255—259°. Boiling water dissolves it somewhat sparingly to form a brownish-red solution, which with alkali becomes orange-yellow coloured, and gives with lead acetate a greenish-brown precipitate closely resembling that yielded by an extract of the red cotton petals with this reagent. If gossypitrone suspended in warm water is treated with dilute sulphurous acid solution, a clear, yellow liquid rapidly results, and ultimately becomes semi-solid owing to the separation of needles. From an aqueous solution of these on boiling, crystals separated which melted at 240—242° and had all the properties of gossypitrin. Gossypitrone is evidently, therefore, the quinone of gossypitrin.

Interesting is the fact that gossypitrone dyes aluminium mordanted calico pretty green shades, which are very similar to those given by an extract of the red cotton petals. It is quite possible that the original shade may be blue, for gossypitrone undergoes reduction during the dyeing operation, and indeed the green-dyed portions referred to gradually become yellow on keeping. Experiments with mordanted woollen cloth gave shades which are identical with those produced by gossypitrin, and that these represent the dyeing property of the glucoside itself is clear owing to their general similarity to those given by quercimeritrin in a similar manner:

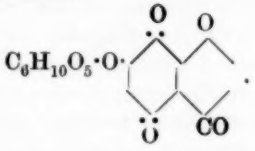
Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Reddish-brown.	Dull yellow.	Bright orange.	Dark olive-brown.

In the earlier stages of the dyeing operation the shade produced on the aluminium mordanted wool possessed a decided green tint, but this gradually altered as the temperature of the dye-bath was raised. Whereas, therefore, when dyed gossypetin passes into its quinone gossypitone, gossypitrone, the oxidation product of gossypitrin in these circumstances suffers the reverse change.

If a solution of gossypitrone in hot water is treated with 7 per cent. of sulphuric acid and heated to boiling, the red liquid becomes first brighter and then subsequently paler in colour. On keeping, a pale brown, crystalline powder separates, which is readily soluble

in alcohol, and from this solution, when concentrated, ether deposits a trace of a reddish-brown, amorphous substance resembling gossypitone. Here, again, reduction evidently occurs, the main product being gossypetin, and this is unfortunate, for although gossypitrone, judging by its method of formation, would appear to be the glucoside of gossypitone, actual proof in this respect is lacking.

The dyeing properties of gossypitrin indicate that the sugar group is attached to the tetrahydroxybenzene nucleus, it being somewhat analogous in this respect to quercimeritrin. The nature of this tetrahydroxybenzene nucleus is uncertain, although should this prove to be a dihydroxyquinol, a para-quinonoid grouping in gossypitrone is not impossible:



To determine this point, enzyme hydrolysis naturally suggests itself, which will be studied when an opportunity occurs. These experiments, however, indicate that although a certain resemblance exists between gossypitrone and the colouring matter of the red petals of the cotton flower, this is apparently but a coincidence. The behaviour of gossypitrone when hydrolysed by acid proves it to be in no way connected with the red, amorphous compounds here described, which would appear more probably to consist of alteration products of the anthocyanin originally existing in the flower.

The author is indebted to Mr. Isaac Shulman for his assistance in the earlier stages of this work.

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XIV.—*Non-aromatic Diazonium Salts. Part V. Diazo-derivatives of Aminotriazoles.*

By Gilbert T. Morgan and Joseph Reilly.

The aminotriazoles furnish an instance of a group of non-aromatic heterocyclic bases which undergo diazotisation, the researches of Thiele and Manchot having indicated that in hydrochloric acid solution these amines yield diazo-derivatives coupling with aromatic bases, such as β-naphthylamine (*Annalen*, 1898, **303**, 41).

Two points of interest were noted under these experimental conditions: first, that the diazo-compound was very unstable in the presence of hydrochloric acid, and secondly, that its coupling power disappeared when the solution was rendered alkaline. The first of these changes, which occurred rapidly even in ice-cold solution, led to the elimination of diazo-nitrogen and to the production of a chlorotriazole. The loss of coupling power which occurred on rendering the solution alkaline was assumed to be due to the formation of an *iso*diazo-compound, but this substance was neither identified nor isolated by the foregoing investigators.

In connexion with the general problem of the diazotisability of non-aromatic bases we have studied the behaviour of the aminotriazoles towards diazotising agents with the following results.

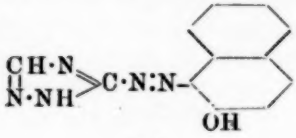
The work of Thiele and Manchot (*loc. cit.*) was in the main confirmed as regards the instability of the diazo-derivative in the presence of aqueous or alcoholic hydrochloric acid; the diazo-nitrogen is evolved at the ordinary temperature with the production of the corresponding chlorotriazole. A far more favourable result is obtained, however, by diazotising in the presence of an oxy-acid. When treated with sodium or ethyl nitrite, a cold dilute nitric acid solution of 5-amino-3-methyl-1:2:4-triazole yields a stable diazo-derivative coupling with β-naphthol, which can be isolated in the form of the sparingly soluble *5-diazo-3-methyl-1:2:4-triazole aurichloride*, $C_3H_3N_5,H_2O,AuCl_3$. 5-Amino-1:2:4-triazole when similarly diazotised and treated with gold chloride yields *5-diazo-1:2:4-triazole aurichloride*, $C_2HN_5,AuCl_3$.

A remarkable change occurs on evaporating at the ordinary temperature the nitric acid solution of 5-diazo-3-methyl-1:2:4-triazole. There is no loss of diazo-nitrogen during concentration, but the white, crystalline, soluble residue no longer couples with alkaline or alcoholic β-naphthol. This product still, however, contains the nitrogen requisite to form a diazonium salt, for when

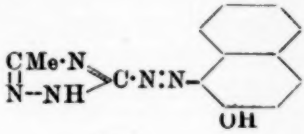
dissolved in concentrated nitric acid or preferably sulphuric acid it is reconverted into a directly coupling diazo-derivative, which condenses quantitatively with β-naphthol.

A similar result is observed on diazotising 5-amino-1:2:4-triazole, but in the case of the simpler base the products are less stable.

Unlike the purely aromatic azo-β-naphthols, 1:2:4-*triazole*-5-*azo*-β-*naphthol* (I) and 3-*methyl*-1:2:4-*triazole*-5-*azo*-β-*naphthol* (II)



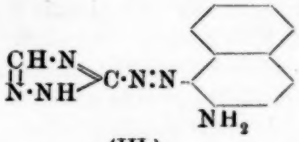
(I.)



(II.)

are soluble in dilute aqueous alkali hydroxides.

This solubility in aqueous alkali is in all probability due to the presence in the triazole ring of an imino-group contiguous to the carbon atom bearing the azo-complex. That the hydroxylic hydrogen of the aromatic group is not involved in this salt formation is demonstrated by the fact that 1:2:4-*triazole*-5-*azo*-β-*naphthylamine* (III) is also readily soluble in aqueous alkali hydroxides:



(III.)

The acidic character of the iminic hydrogen atom probably plays also an important part in determining the formation of the aurichlorides from the triazolediazonium salts and in the transformation of these diazonium compounds into *iso*diazo-derivatives.

The diazo- and *iso*diazo-derivatives of the triazole series are being further examined.

Experimental.

Diazotisation of 5-Amino-3-methyl-1:2:4-triazole.

The starting point in the preparation of 5-amino-3-methyl-1:2:4-triazole was aminoguanidine nitrate or the corresponding hydrochloride or carbonate, the two latter salts being converted into the nitrate by double decomposition with silver nitrate or nitric acid respectively.

Ten grams of aminoguanidine carbonate were converted into nitrate by evaporation to dryness on the water-bath with the calcu-

lated quantity of nitric acid. Excess of nitric acid led to destructive oxidation. The nitrate was heated with water (20 c.c.) and glacial acetic acid (10 c.c.) in a reflux apparatus, the product being kept in solution by adding water or dilute acetic acid. After twenty-four hours the reaction was completed, the solution evaporated to dryness, and the resulting anhydrous acetylaminoguanidine nitrate then melted at 144°, the hydrated salt melting at 85°. This salt was then dissolved in water, the solution evaporated to dryness with an equivalent amount of sodium carbonate (0·5 mol.), the residue extracted repeatedly with absolute alcohol, the alcohol distilled from the extract, and the residual, crude triazole purified by extraction with ethyl acetate in a Soxhlet apparatus. 5-Amino-3-methyl-1 : 2 : 4-triazole (m. p. 148°) was thus obtained in quantitative yield.

Diazotisation in Hydrochloric Acid.—On adding aqueous sodium nitrite to a solution of 5-amino-3-methyl-1 : 2 : 4-triazole in cold dilute hydrochloric acid, a diazonium chloride was obtained which decomposed rapidly even in solution, and on stirring the ice-cold liquid there was a rapid evolution of nitrogen.

Ethyl nitrite in moderate excess was added to 5-amino-3-methyl-1 : 2 : 4-triazole dissolved in cold alcoholic hydrochloric acid and the solution concentrated in a vacuum over potassium hydroxide and calcium chloride, when 5-chloro-3-methyl-1 : 2 : 4-triazole (m. p. 147°) slowly separated as a bulky, white precipitate (compare Thiele and Manchot, *loc. cit.*).

Diazotisation in Nitric Acid.—The substitution of nitric acid for hydrochloric acid in the diazotisation of 5-amino-3-methyl-1 : 2 : 4-triazole with sodium nitrite in aqueous solution led to the production of a much more stable diazonium salt. The solution, which was free from effervescence, was poured into alcoholic β-naphthol, when a brownish-red azo-compound separated. This substance was purified by four crystallisations from dilute ethyl alcohol (50 per cent.) and finally from absolute alcohol, when it was obtained in dark orange-brown plates and flattened needles melting at 213—215° :

0·0835 gave 20·4 c.c. N_2 at 20° and 737 mm. N = 27·74.

$C_{13}H_{11}ON_5$ requires N = 27·67 per cent.

3-Methyl-1 : 2 : 4-triazole-5-azo-β-naphthol was very readily soluble in ethyl acetate, chloroform, or in methyl or ethyl alcohol, less so in acetone or glacial acetic acid, and dissolved only sparingly in ether. With concentrated sulphuric acid it developed a purple coloration. Unlike the purely aromatic azo-β-naphthols, this mixed azo-derivative dissolved readily in cold dilute potassium hydroxide to a brownish-red solution.

5-Diazo-3-methyl-1 : 2 : 4-triazole Aurichloride.—A concentrated

aqueous solution of gold chloride was slowly added to 5-amino-3-methyl-1:2:4-triazole diazotised with sodium nitrite in dilute nitric acid; the aurichloride separated slowly as a heavy, crystalline precipitate consisting of rosettes of small, bright yellow prisms, the yield being almost quantitative. The salt, which was quite stable at the ordinary temperature, exploded on heating quickly to 100°. On raising the temperature slowly, it decomposed with brisk effervescence:

0·2300 gave 33·3 c.c. N_2 at 20° and 764 mm. N = 16·84.
0·1639 „ 0·1616 AgCl. Cl = 24·30.
0·1647 „ 0·075 Au. Au = 45·50.

$C_3H_5ON_5,AuCl_3$ requires N = 16·26; Cl = 24·73; Au = 45·76 per cent.

Although quite stable when dry, the sparingly soluble aurichloride changed in aqueous solution to an intensely red substance resembling an azo-derivative.

3-*Methyl*-1:2:4-*triazole*-5-iso*diazohydroxide* was obtained by diazotising 5-amino-3-methyl-1:2:4-triazole with excess of ethyl nitrite in dilute nitric acid, the solution being allowed to evaporate to dryness over potassium hydroxide at the ordinary temperature. The colourless, crystalline residue, which could be dried at 100° unchanged, but intumesced at 120°, dissolved readily in water and was less soluble in methyl or ethyl alcohol.

When crystallised from the latter solvent the *iso*diazo-derivative separated in colourless, prismatic needles, which after drying at the ordinary temperature in a vacuum desiccator contained 40·20 per cent. of nitrogen. This percentage is too low for the *iso*diazohydroxide, $C_3H_5ON_5$, but corresponds approximately with this substance in combination with one molecular proportion of alcohol (N = 40·46 per cent.).

This product did not couple with β-naphthol in alcoholic or alkaline solutions, but when dissolved in moderately concentrated nitric acid (2 vols. of acid of D 1·42 + 1 vol. of water) or preferably in cold concentrated sulphuric acid it became converted into a normal diazonium salt which on diluting the strong acid with cold water coupled with alcoholic β-naphthol, the formation of the azo-derivative being hastened by the addition of sodium acetate. This azo-compound, which was evidently 3-methyl-1:2:4-triazole-5-azo-β-naphthol, gave with concentrated sulphuric acid the same bluish-crimson coloration as that developed from the preparation obtained directly from 3-methyl-1:2:4-triazole-5-diazonium nitrate and alcoholic β-naphthol.

Diazotisation of 5-*Amino*-1 : 2 : 4-*triazole.*

The preparation of 5-amino-1 : 2 : 4-triazole from aminoguanidine nitrate followed the same course as that of its 3-methyl derivative, excepting that formic acid was substituted for acetic acid in the acylation. Formylaminoguanidine nitrate was similarly converted into 5-amino-1 : 2 : 4-triazole by the action of aqueous sodium carbonate.

Diazotisation in Hydrochloric Acid.—When treated in dilute hydrochloric acid with either sodium or ethyl nitrite, 5-amino-1 : 2 : 4-triazole was converted into an unstable diazonium chloride, readily losing nitrogen even in ice-cold solutions to yield 5-chloro-1 : 2 : 4-triazole (m. p. 167°).

Diazotisation in Nitric Acid.—Diazotisation of 5-amino-1 : 2 : 4-triazole in dilute nitric acid with either sodium or ethyl nitrite gave a stable diazo-solution, from which nitrogen was not evolved in the cold. The solution added to alcoholic β-naphthol (1 mol.) produced a copious precipitate of azo-derivative, which was washed with hot alcohol and crystallised from methyl alcohol, when it separated in acicular, orange crystals melting at 252—255°:

0·0578 gave 0·1284 CO_2 and 0·0222 H_2O. C = 60·55; H = 4·25.

0·0880 „ 23 c.c. N_2 at 20° and 737 mm. N = 29·64.

$C_{12}H_9ON_5$ requires C = 60·25; H = 3·76; N = 29·30 per cent.

1 : 2 : 4-*Triazole*-5-*azo*-β-*naphthol* was only sparingly soluble in the ordinary organic media; it gave a bluish-purple coloration with cold concentrated sulphuric acid and dissolved readily in cold dilute aqueous potassium hydroxide to a brownish-red solution.

1 : 2 : 4-*Triazole*-5-*azo*-β-*naphthylamine* was prepared by adding a solution of 1 : 2 : 4-triazole-5-diazonium nitrate free from excess of nitrous acid to alcoholic β-naphthylamine, when it separated as a dark red precipitate, rendered paler in colour by ammonia. This azo-β-naphthylamine was sparingly soluble in chloroform, benzene, and methyl or ethyl alcohol. When crystallised from ethyl acetate, it separated in dark brownish-red plates melting at 243—245°:

0·1585 gave 0·3527 CO_2 and 0·0672 H_2O. C = 60·68; H = 4·73.

0·0939 „ 29·1 c.c. N_2 at 19° and 737 mm. N = 35·28.

$C_{12}H_{10}N_6$ requires C = 60·50; H = 4·20; N = 35·29 per cent.

1 : 2 : 4-Triazole-5-azo-β-naphthylamine developed an intense brownish-yellow coloration with cold concentrated sulphuric acid, becoming red on dilution. In cold dilute aqueous potassium hydroxide, it dissolved readily to a brownish-yellow solution.

5-*Diazo*-1 : 2 : 4-*triazole Aurichloride.*—Slightly more than the calculated quantity of gold chloride was slowly added to 5-amino-1 : 2 : 4-triazole diazotised with sodium nitrite in dilute sulphuric

acid. The aurichloride, which separated in opaque, yellow, granular crystals, was washed repeatedly with cold water and dried on a porous tile in a desiccator over sulphuric acid:

0·2088 gave 0·2265 AgCl. Cl = 26·81.

0·2158 ,, 33·2 c.c. N_2 at 21° and 756 mm. N = 17·72.

0·1786 ,, 0·0884 Au. Au = 49·45.

$C_2HN_5,AuCl_3$ requires Cl = 26·71; N = 17·55; Au = 49·46 per cent.

Evidence was obtained of the formation of 1:2:4-*triazole*-5-iso*diazohydroxide*, although the substance was not isolated in a purified condition. 5-Amino-1:2:4-triazole was diazotised in dilute nitric acid and sodium acetate was added to the solution, when a yellowish-white precipitate was slowly produced which was less crystalline than its homologue from 5-amino-3-methyl-1:2:4-triazole. After washing and drying at the ordinary temperature the substance contained 60·31 per cent. of nitrogen, the calculated proportion for 1:2:4-triazole-5-*iso*diazohydroxide being 61·8. Further experiments on the foregoing *iso*diazo-derivatives are in progress.

We are indebted to Professor W. Caldwell and Mr. W. F. Woodworth for their assistance, and we desire to express our thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
DUBLIN. [*Received, January 14th*, 1916].

XV.—*The Influence of Different Surfaces on the Decomposition of Methane.*

By WILFRID ERNEST SLATER.

THE thermal decomposition of methane, in its incipient stages, has been generally considered as a purely surface effect, the rate of dissociation into carbon and hydrogen being regarded as proportional to the amount of heated surface exposed to the gas and independent of the nature of that surface (compare Bone and Coward, T., 1908, **93**, 1197).

In some recent work on the decomposition of methane in the presence of silica (Campbell and Slater) it was found that the rate of dissociation at temperatures of 900° to 1000° was increased beyond what was expected on the above assumption. Thus, when pieces of (*a*) silica tubing, and (*b*) glazed porcelain tubing of the

same size and shape were respectively exposed to the gas under the same conditions of temperature and pressure, the amount of dissociation in a given time using (*a*) was greater than the amount for the time using (*b*).

It thus appeared that some additional effect arising from the chemical or physical nature of the surface employed must be present, and it was reasonable to suppose that any other substance might exert a similar specific influence on the reaction.

A series of experiments with various substances was therefore carried out in the manner and with the results described.

Experimental.

The principle of the experiments was the exposure of an equal surface of each substance in turn to the action of pure methane under the same conditions of temperature and pressure and for the same length of time, the extent of the decomposition being measured by the amount of hydrogen found on analysing the residual gases.

The choice of materials was necessarily limited, owing to the high temperature and the nature of the reaction. The following were taken as fairly representative:—

(1)	(2)	(3)
Silica (quartz)	Wood charcoal	Iron
Alumina (anhydrous (Al_2O_3)	Graphite	Copper
Magnesia (MgO)	Carborundum (SiC)	
Lime (CaO)		
Baryta (anhydrous BaO)		

Each was used in the form of a fine powder, obtained by prolonged grinding in a mortar and sifting through fine gauze. In the case of iron, ordinary filings were ground, sifted, and re-ground until in the same state of division as the rest. The copper was obtained in the first instance in the finely-divided form, and was used in this condition.

The methane was prepared and purified by Campbell and Parker's method (T., 1913, **103**, 1292) from aluminium carbide and water. Analysis of the gas gave $CH_4 = 99{\cdot}4$ per cent., the rest being nitrogen.

Apparatus.—The apparatus employed is shown in the diagram.

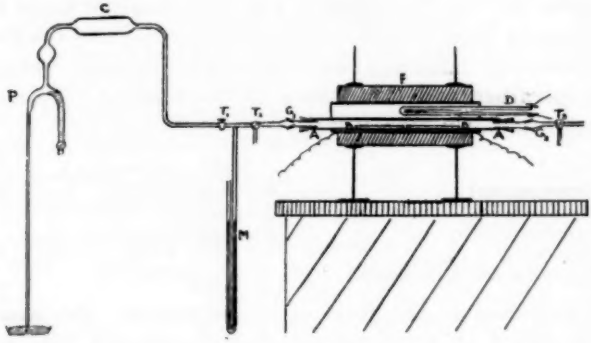
It consists essentially of an electric platinum-wound tube-furnace *F*, through which passes the tube *A A* of Berlin porcelain (glazed inside and outside), of length 58 cm. and internal bore 1 cm. This tube is connected, at one end through the ground-glass joint G_1, the three-way tap T_2, and the two-way tap T_1 with the mercury pump *P*; and at the other through the joint G_2 and the three-way tap T_3 with the methane gas-holder. Between T_1 and T_2 is the

manometer M; and between T_1 and the pump is the bulb C, making the volume of the apparatus to the left of T_1 about double that to the right.

$B\,B$ are two porcelain boats containing the powdered substance, placed end to end along the middle portion of the tube $A\,A$. By this means an equal volume of gas was displaced in each experiment, and an equal surface of the substance exposed to the gas. Care was always taken to have the boats in exactly the same position throughout.

The temperature of the furnace was indicated by a thermo-couple pyrometer D, the end of which was placed in the centre of the furnace-tube.

Method of Procedure.—The experiment was conducted as follows: The two boats, filled level with the upper edge with the powdered substance, were carefully pushed into the porcelain tube through



the joint G_2. The apparatus was then closed, the pump started, and the whole exhausted, the furnace becoming heated in the meantime. When quite exhausted, the apparatus was tested for possible leakages by closing T_1 and allowing to remain a few minutes while the temperature of the furnace was adjusted by means of a variable resistance. There being no leakage, gas was admitted through T_3 (the time being carefully noted by means of the seconds hand of a watch) in such a manner that the whole space between T_3 and T_1 was filled in about five seconds, the speed being judged by the rate of fall of the mercury in M. Immediately the pressure reached atmospheric, T_3 was closed and the reaction allowed to proceed for the required time (five or ten minutes). At the end of that time T_1 was opened for an instant, thus allowing most of the gas to be drawn over into the vacuous portion between T_1 and P. T_1 being again closed, T_2 was opened to the air, and a stream of

oxygen passed through T_3 to burn off the deposit of carbon in $A\ A$. Lastly, a sample of the gas in P was pumped out and analysed, and the apparatus prepared for the next experiment.

Each experiment was performed in duplicate, and in some cases was repeated three or four times without intermission. In each case a rough check on the result was obtained by observing the manometer during the experiment. Thus, in cases where the rate of decomposition was great (for example, when using iron or charcoal), the internal pressure increased very considerably, whereas in others the increase was slight.

Owing to inevitable breakages, parts of the apparatus had to be

Results.

1st Series:—

Temperature 910°: Time five mins
CH_4=99·4 per cent.

Substance.	Percentage of hydrogen found. Actual.		Mean.
Tube empty	(*a*) 10·9	(*b*) 11·1	11·0
Silica	(*a*) 8·6	(*b*) 8·8	8·7
Magnesia	(*a*) 11·2	(*b*) 11·6	11·4
Quicklime	(*a*) 15·0	(*b*) 16·2	15·6

2nd Series:—

Temperature 910°: Time ten mins.
CH_4=99·6 per cent.

Substance.	Percentage of hydrogen found. Actual.		Mean.
Tube empty	(*a*) 15·9	(*b*) 16·4	16·2
Silica	(*a*) 12·5	(*b*) 12·1	12·3
Magnesia	(*a*) 12·2	(*b*) 11·8	12·0
Quicklime	(*a*) 23·6	(*b*) 24·3	23·9
Alumina.....	(*a*) 10·7	(*b*) 10·1	10·4
*Baryta	(*a*) 6·7	(*b*) 6·3	6·5
Charcoal	(*a*) 34·4	(*b*) 33·4	33·9

3rd Series:—

Temp. 910°: Time ten mins.
CH_4=99·4 per cent.

Tube empty	(*a*) 10·4	(*b*) 9·9	10·1
Quicklime	(*a*) 35·3	(*b*) 35·1	35·2
Charcoal	(*a*) 68·6	(*b*) 70·2	69·4
Iron	(*a*) 72·1	(*b*) 74·1	73·1

4th Series:—

Temp. 910°: Time ten mins.
CH_4=99·6 per cent.

Tube empty	(*a*) 17·9	(*b*) 18·1	18·0
Silica	(*a*) 15·2	(*b*) 14·9	15·0
Graphite	(*a*) 65·6	(*b*) 66·4	66·0
Carborundum ...	(*a*) 43·4	(*b*) 44·6	44·0
Copper	(*a*) 28·1	(*b*) 27·8	27·9

* The baryta underwent fusion and possibly some chemical change in the process.

renewed from time to time, and this involved small changes of volume. Only, therefore, the results of experiments during which no such change occurred (namely, those in the same series in the following table) are strictly comparable; but the blank experiments conducted after each such change give results sufficiently near to justify inter-comparison and the consequent conclusion that each substance tends to exert a specific influence on the rate of decomposition—apparently by virtue only of its chemical or physical nature.

The residual gas throughout was found to contain nothing but methane, hydrogen, and a trace of nitrogen.

These results, whilst of no value as regards the actual rate of decomposition in each case, yet appear to indicate that the rate depends, not merely on the amount of heated surface exposed to the gas, but also on the nature of the substance of which the surface is composed.

It is already known that the rate of combination of carbon and hydrogen at 500—520° under pressure is influenced by the presence of nickel and certain metallic oxides (Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 433), and the two prenomena may be connected.

I am indebted to Prof. H. B. Dixon, F.R.S., for the use of laboratory, apparatus, and materials.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, MANCHESTER. [*Received, January 13th*, 1916.]

XVI.—*Amphoteric Metallic Hydroxides. Part III. Chromium Hydroxide.*

By JOHN KERFOOT WOOD and VERA KATHLEEN BLACK.

THE well-known fact that, on the addition of a solution of sodium hydroxide to one of a chromic salt a precipitate is obtained which is soluble in an excess of the precipitant, would, at first sight, appear to point conclusively to the possession by chromic hydroxide of an acidic as well as of a basic character. This, indeed, is the way in which the above reaction is interpreted in most, if not all, modern text-books. Further, the existence of compounds of chromic oxide with the oxides of bivalent metals, of which compounds chrome iron ore, $FeCr_2O_4$, is by far the most important, might be considered to support this view, all the more so as these

substances are isomorphous with spinel, which contains the analogous and undoubtedly amphoteric compound, alumina. Doubt has been thrown on the above explanation, however, as a result of the work of Herz and others. Herz (*Zeitsch. anorg. Chem.*, 1901, **28**, 344) drew attention to the difference in behaviour shown by freshly precipitated chromic hydroxide and the same substance after it had been washed and dried in a desiccator; the latter specimen was found to be almost insoluble in a solution of sodium hydroxide. The difference in properties was attributed by Hantzsch (*Zeitsch. anorg. Chem.*, 1902, **30**, 338) to a difference in the degree of hydration of the samples, and the gradual precipitation which takes place when alkaline solutions of chromic hydroxide are kept was attributed to a transformation of the freshly precipitated variety into the more stable and less soluble modification, the chromium compound, during the process of transition, being considered to exist largely in a colloidal condition. In later papers, Herz and Fischer (*Zeitsch. anorg. Chem.*, 1902, **31**, 354; 1904, **40**, 39), from experiments involving dialysis and determinations of electrical conductivity, expressed the opinion that the alkaline solutions of chromic hydroxide are really colloidal solutions, and that no compounds analogous to aluminates are produced. Kremann (*Zeitsch. anorg. Chem.*, 1902, **33**, 87), on the other hand, also as a result of dialysis experiments, drew the conclusion that chromites have an actual existence. In a recent paper Nagel (*J. Physical Chem.*, 1915, **19**, 569) supports the view of Herz and Fischer, so it will be seen that, in spite of the apparent simplicity of the problem, there is a considerable amount of uncertainty as to whether chromic hydroxide is or is not possessed of an amphoteric character.

For some time past, in continuation of the work described by one of us (T., 1908, **93**, 411; 1910, **97**, 878), experiments have been in progress with a view to the elucidation of the character of chromic hydroxide. The results obtained, and described in the present paper, seem to show quite conclusively that chromic hydroxide is of an amphoteric nature.

Experimental.

The starting-point of the experiments was chrome alum, supplied by Kahlbaum. Chromic hydroxide was prepared from this by precipitation with ammonia and, after thorough washing, was introduced into bottles of "resistance" glass along with solutions, of varying concentration, of sodium hydroxide. The bottles were placed in a thermostat at 25° and periodically shaken. After about three weeks, a portion of the liquid containing the largest concentration of alkali was removed and analysed, but was found

to contain only a very small quantity of chromium. The solutions were accordingly left in the thermostat for a longer period, while other work was in progress, in order to ascertain whether any further amount of chromic hydroxide would pass into solution. After nearly two months from the commencement of the experiments, it was observed that the most alkaline liquid was acquiring a yellow colour. This suggested the presence of chromate, and accordingly, portions were filtered and tested (*a*) by acidifying and shaking with ether and hydrogen peroxide, (*b*) by acidifying and adding potassium iodide and starch; both tests gave a positive result. In the course of time, the contents of the other bottles also acquired a yellow colour, the intensity of colour being more or less proportional to the alkalinity of the solution. It would appear, then, that chromic hydroxide, when left in contact with a solution of sodium hydroxide, is, at 25°, very slowly converted into sodium chromate, the necessary oxygen being presumably supplied by the air. Although it is well known that alkaline oxidising agents convert chromic hydroxide into chromates, the formation of the latter, under the conditions employed by the authors, does not appear to have been noticed previously.

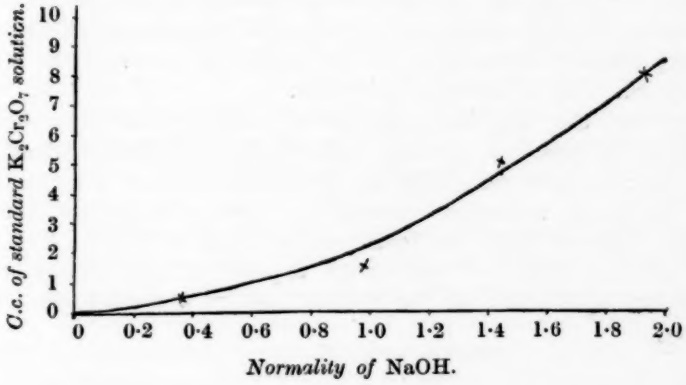
In view of the results obtained, all the materials used were tested for the presence of impurities of an oxidising nature, but in every case with negative results.

Two mixtures of chromic hydroxide and sodium hydroxide were prepared, the only difference between them being that in one case boiled water was employed in making up the mixture, whilst with the other ordinary distilled water was used; the bottle containing the former was filled up to the stopper, but the other bottle was only half-full. In the course of time, chromate developed in the latter, but no production of chromate was noticed in the full bottle, thus showing the part taken in the process by the air.

Fresh experiments were commenced to ascertain whether the same change would take place, and again, and in about the same time, the contents of the bottles became yellow, the colour first appearing in the most alkaline mixture, and last in the least alkaline one. In the last series of experiments, each of the bottles containing the mixture of alkali and chromic hydroxide was fitted with a soda-lime tube, the other end of which was open to the air; with this exception, the experiments were carried out in the same manner as the earlier ones, and, as already indicated, with similar results. The relative intensity of colour of the filtered solutions gave a rough indication of the amounts of chromate present, but it was thought desirable to attempt a more accurate method of estimation. The method described by van Eck (*Chem.*

Weekblad, 1915, **12**, 6), by which, it is said, chromates may be estimated colorimetrically by means of tartaric acid and α-naphthylamine was tried, but was found unsuitable because of the somewhat fugitive nature of the colour produced. A more satisfactory method was found to consist in the comparison of the colour produced on the addition of potassium iodide to the filtered solution acidified with sulphuric acid with that given under similar conditions by a standard solution of potassium dichromate. The results of one such series of determinations are given in the following table, the figures in the second column giving the volume of standard solution of dichromate (0·1 gram of chromium per

FIG. 1.



litre) equivalent to 10 c.c. of the solution examined, whilst in the third column is indicated the concentration of alkali in the solution.

Mixture *A*	8·0	1·93*N*
Mixture *B*	5·0	1·44*N*
Mixture *C*	1·5	0·98*N*
Mixture *D*	0·7	0·45*N*

The amounts of chromate found in the different solutions were found to correspond closely with the relative amounts as deduced from the colour intensity of the filtered mixtures; the solutions are, of course, very dilute, the most concentrated containing rather less chromium than a 0·005*N*-solution of potassium dichromate. The curve obtained by plotting the above results is shown in Fig. 1; similar curves were obtained by plotting the results from other series of experiments. It is quite evident that, although the amount of chromate formed is small, the concentration of chromate in the solution is dependent on the concentration of alkali.

With regard to the interpretation of these results, it appears to

the authors that the only possible explanation is to be found in the possession of a certain degree of acidic character by the chromic hydroxide; in view of the conditions of experiment, there can be no possibility of the formation of colloidal solutions of the hydroxide, and accordingly, the chromium must be present in the form of chromite. This chromite would then undergo oxidation to chromate by the oxygen of the air, and, the equilibrium being thereby disturbed, more chromium hydroxide would pass into solution, and in its turn become oxidised, and so the process would go on until the solution acquired a yellow colour as a result of the chromate produced. Naturally, the quantity of chromite formed will depend on the concentration of the alkaline solution employed, and, accordingly, the most alkaline solution would be the one in which the development of chromate would first be noticed. These conclusions are not invalidated by the small quantity of chromium actually present in the solutions, the reason for which is the very sparing solubility of chromic hydroxide.

Moreover, the very small amount of chromic hydroxide which is apparently dissolved by even a $2N$-solution of sodium hydroxide does not necessarily mean that the hydrolysis constant is large and that the acidic ionisation constant of chromic hydroxide is not sensibly different from the ionisation constant of water. This is quite evident from the well-known expression representing the hydrolysis equilibrium of the sodium salt of a mono-basic acid, namely,

$$\frac{[\mathrm{NaOH}] \times [\mathrm{Acid}]}{[\mathrm{Salt}]} = \text{const.}$$

for evidently the quantity of salt which can exist in solution in presence of a given concentration of alkali depends on the solubility of the acid, which represents its maximum active mass, as well as on the magnitude of the hydrolysis constant; if the solubility of the acid in water is very small, as must necessarily be the case for chromic hydroxide, the ratio [NaOH]/[Salt] will, for a given value of the constant, be correspondingly large.

In the opinion of the authors, therefore, it seems to be undoubtedly established that chromites do exist in an alkaline solution of chromic hydroxide; when the solution is freshly prepared and is kept a little time, part of the dissolved hydroxide separates out in a less soluble form, and probably does, during this period of transition, exist for a time in the colloidal condition, but when all such precipitation has taken place, a small amount of chromite will still be present in the solution.

Although it is impossible, from the results given, to calculate the acidic ionisation constant of chromic hydroxide, the results

throw a little light upon the constitution of chromites. If sodium chromite had the constitution $ONa{\cdot}Cr(OH)_2$, it would be a salt of a monobasic acid, and the curve showing the relation

$$[NaOH]/[Salt]$$

would be a straight line. All the results showing the relation of alkali to chromate, which latter is proportional to the chromite formed, show that this condition is not fulfilled, and accordingly, it must be concluded that chromic hydroxide behaves as a polybasic acid.

Chromic Hydroxide Considered as a Base.

Determinations of the degree of hydrolysis of chromic chloride, from which it is possible to calculate the basic ionisation constant of chromic hydroxide, have been made by Denham (T., 1908, **93**, 51) and Bjerrum (*Zeitsch. physikal. Chem.*, 1907, **59**, 336), the results obtained, by electrometric measurements, being in close agreement. Attempts were made by the authors to employ the methyl acetate catalysis method for the determination of the hydrolysis of violet solutions of chromic chloride. The chromium chloride was prepared from Kahlbaum's chrome alum by two different methods:—

(*a*) A solution of the chloride was prepared by adding to a solution of chrome alum one containing the calculated quantity of barium chloride and filtering off the precipitated barium sulphate.

(*b*) The solid violet hexahydrated chloride was prepared by the method described by Higley (*J. Amer. Chem. Soc.*, 1904, **26**, 613), and was freed from any traces of the green modification by repeated washing with acetone. The solid was kept in a desiccator, portions being removed as desired for the preparation of the solutions.

The concentration of all solutions was found by analysis. The solution was mixed with freshly distilled methyl acetate, and the velocity of the action, at 25°, compared with that shown by a mixture of hydrochloric acid, potassium chloride, and methyl acetate, the amount of ester and the total concentration of chlorine being the same in the two mixtures. It was soon seen that the solution containing the chromium compound was behaving in an abnormal manner; the velocity of catalysis, as measured by the increase of acidity, was at first small, but gradually increased instead of diminishing as in a normal reaction; after many days the velocity began to fall slightly. This behaviour was noticed with solutions prepared by both the methods described and with both freshly prepared and old solutions. The last fact shows that the phenomenon cannot be due to any gradual change in the chromium chloride solution. It was found that the abnormality

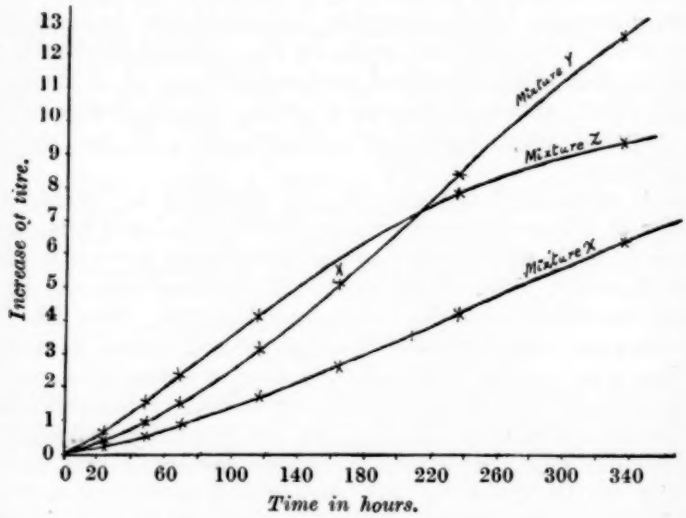
was rather more pronounced with a larger amount of ester present, and that when a little glacial acetic acid was added to the original mixture of chromic chloride and ester, the period of increasing velocity lasted for a very much shorter time, the mixture soon behaving in a more normal manner. The influence of the amount of ester and of the presence of acetic acid is shown in Fig. 2, in which the increase in the titre of three solutions, all containing the same volume of the same solution of chromic chloride (0·0924 *N*), is plotted against the time, measured in hours. The mixtures had the following compositions:—

Mixture *X*. 50 c.c. $CrCl_3$ solution + 2 c.c. H_2O + 3 c.c. $CH_3{\cdot}CO_2Me$.

Mixture *Y*. 50 c.c. $CrCl_3$ solution + 5 c.c. $CH_3{\cdot}CO_2Me$.

Mixture *Z*. 50 c.c. $CrCl_3$ solution + 2 c.c. $CH_3{\cdot}CO_2H$(glacial) + 3 c.c. $CH_3{\cdot}CO_2Me$.

FIG. 2.



The results obtained show that the methyl acetate catalysis is quite unsuitable as a means of determining the degree of hydrolysis of chromic chloride, and it seems probable, from a consideration of the results obtained with the different mixtures, that the cause of the behaviour described is the formation of aceto-chloride or other complex acetic acid derivative of chromium.

Another method somethimes employed in the investigation of the hydrolysis of salts is to determine the solubility of the base in solutions of the acid of varying concentration. As is well known, numerous basic chlorides of chromium have been described, and the varying opinions regarding these did not make it appear prob-

able that the method mentioned would prove a satisfactory one for the investigation of the hydrolysis of chromic chloride. This anticipation was quickly verified when chromic hydroxide was shaken with solutions of hydrochloric acid of varying concentration, for it was found impossible in many cases to obtain definite figures to represent the composition of the various solutions.

The attempts, therefore, to obtain a value for the basic ionisation constant of chromic hydroxide by other methods than have been previously employed were unsuccessful.

The authors desire to express their thanks to the Carnegie Trustees for a grant which covered the cost of the investigation.

UNIVERSITY COLLEGE, DUNDEE,
UNIVERSITY OF ST. ANDREWS. [*Received, January 15th*, 1916.]

XVII.—*The Interaction of Tetranitromethane and Potassium Ferrocyanide.*

By FREDERICK DANIEL CHATTAWAY and JOHN MALTHOUSE HARRISON.

TETRANITROMETHANE readily reacts with potassium ferrocyanide in a saturated aqueous solution, producing the potassium salt of *aci*-trinitromethane, potassium nitrite, and potassium ferricyanide. The action, which may be represented by the equation

$$C(NO_2)_4 + 2K_4FeC_6N_6 = C(NO_2)_2{:}NO{\cdot}OK + KNO_2 + 2K_3FeC_6N_6,$$

proceeds quietly and quantitatively, and the sparingly soluble potassium salt of *aci*-trinitromethane crystallises out in a pure state, the other products remaining in solution.

This reaction affords a safe and easy way of preparing the *aci*-trinitromethane salt; the action of potassium ethoxide on tetranitromethane, the method hitherto used, being, as Macbeth has shown (*Ber.*, 1913, **46**, 2537), liable to give rise to dangerous explosions.

Bromotrinitromethane reacts similarly with potassium ferrocyanide, the bromine atom in this case being removed, and the potassium salt of *aci*-trinitromethane being produced thus:

$$C(NO_2)_3Br + 2K_4FeC_6N_6 = C(NO_2)_2{:}NO{\cdot}OK + KBr + 2K_3FeC_6N_6.$$

The ease with which one nitro-group or one bromine atom can be thus detached from the carbon atom may be due to the relative dimensions of the spaces occupied by the carbon atom and the nitro-groups respectively, these being such as to admit only three

of the latter to approach sufficiently near the centre of attraction of the carbon atom for the maximum attractive force to be exerted upon them.

A fourth group or atom attracted by the carbon, if occupying sufficient space and of suitable configuration, would alter somewhat the relative positions of the groups around the central carbon atom and force them to a greater distance from the centre of attraction, where they would be less firmly held. As a consequence, one might be more or less easily detached by a suitable reagent.

Such reagents would, however, not be able to bring about interaction if the spaces occupied by the attached groups or atoms were less and they were consequently nearer the centre of attraction and more firmly held.

The latter condition is apparently present in trichloropicrin and tribromopicrin, which do not react with potassium ferrocyanide as do tetranitromethane and bromotrinitromethane.

Experimental.

Interaction of Potassium Ferrocyanide and Tetranitromethane.

Ninety grams of potassium ferrocyanide were dissolved in 300 c.c. of water and shaken vigorously with 3 grams of tetranitromethane. The pale yellow solution became at once of an intense yellow colour, which changed to brown as the action proceeded, and potassium *aci*trinitromethane almost immediately began to separate as a yellow, crystalline powder. After about an hour's shaking, when the odour of tetranitromethane had disappeared, the potassium *aci*trinitromethane was filtered off. The filtrate was now saturated with this salt, and, in order to ascertain the yield from a given quantity of tetranitromethane, 10 grams more were added, and the shaking continued for a little over an hour, until the whole had disappeared. The potassium *aci*trinitromethane which crystallised out was separated by filtration, washed twice with a little distilled water, then twice with alcohol, and, after a short exposure in a vacuum desiccator, was weighed, when 9·4 grams were obtained, the amount theoretically obtainable from 10 grams of tetranitromethane being 9·6 grams. No gas or nitrous fumes or hydrocyanic acid was evolved during the reaction, nor did the liquid become acid. The filtrate from the potassium *aci*trinitromethane, which still contained a considerable quantity of potassium ferrocyanide, was then shaken with 30 grams more of tetranitromethane for several hours until no further action appeared to take place. The potassium *aci*trinitromethane was filtered off, the excess of tetranitromethane

separated, and the liquid, after evaporation to about half its bulk in a vacuum at a slightly raised temperature, examined.

It was found to be neutral and to contain, in addition to a little dissolved potassium *aci*trinitromethane, potassium nitrite and potassium ferricyanide.

On adding dilute sulphuric acid to a small portion, nitrous fumes were liberated in quantity, and on concentrating the remainder, further potassium ferricyanide crystallised out. This was identified by a volumetric estimation, by the shape of the crystals, and by its well-known reactions.

The potassium in the potassium *aci*trinitromethane was estimated by decomposing a weighed amount with sulphuric acid and weighing the potassium sulphate produced. In order to show its purity, the salt, as it at first separated after having been twice washed with water, twice with alcohol and dried, was analysed. (Found K = 20·50.) .

The potassium was also estimated in a specimen of the same salt once recrytallised from water (Found K = 20·66. CO_6N_3K requires K = 20·67 per cent.)

To prepare a small quantity of potassium *aci*trinitromethane, it is best to use a slight excess of potassium ferrocyanide.

If 10 grams of tetranitromethane, which is a convenient amount to use, are shaken for about an hour with a solution of 50 grams [$C(NO_2)_4 : 2K_4FeC_6N_6 = 10 : 44$] of crystallised potassium ferrocyanide in 150 c.c. of water, about 8 grams of pure dry potassium *aci*trinitromethane are usually obtained.

Interaction of Potassium Ferrocyanide and Bromotrinitromethane.

Bromotrinitromethane (1 mol.) was shaken with a saturated aqueous solution of potassium ferrocyanide (2 mols.). It reacted, as far as could be judged, as readily as tetranitromethane. The pale yellow solution became of an intense yellow colour, which quickly changed to brown; potassium *aci*trinitromethane was deposited in small, yellow crystals, and potassium ferricyanide and potassium bromide were produced and remained in solution. The potassium *aci*trinitromethane was collected, and was obtained pure by washing twice with distilled water and twice with alcohol. The potassium was estimated in a specimen thus prepared. (Found K = 20·43. CO_6N_3K requires K = 20·67 per cent.)

Similar experiments were carried out with chloropicrin and bromopicrin. These compounds were found to have no action on a solution of potassium ferrocyanide. After shaking, continued for many hours, no salt separated, nor did any visible action take

place in either case, and the chloropicrin and bromopicrin were found at the end unaltered. After allowing them to remain for several weeks in contact with saturated solutions of potassium ferrocyanide, they were similarly found to be unchanged.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD. [*Received, January 3rd,* 1916].

XVIII.—*Note on the Preparation of Diethylamine.*

By WILLIAM EDWARD GARNER and DANIEL TYRER.

SINCE Wurtz and Hofmann discovered the compound ammonias more than sixty years ago, no very direct method has been worked out which will easily give pure diethylamine in large quantities. Although pure diethylamine can be obtained by the action of sodium hydroxide on *p*-nitrosodiethylaniline, the process is somewhat lengthy, and it was therefore worth while to see whether Hofmann's original method, where an alkyl haloid is allowed to react with ammonia, might be modified so as to give pure diethylamine. Hofmann states that he was unable to separate the mixture of mono-, di-, and tri-ethylamine, but the authors have found that almost pure diethylamine can be prepared without any difficulty by fractional distillation from a mixture of the three bases.

EXPERIMENTAL.

As a result of preliminary experiments, the following method was found to give the best results: A mixture of 8000 c.c. of alcohol and 3000 grams of ethyl bromide was saturated with ammonia several times during the day; the temperature of the mixture gradually rose to about 30°, and after some time the ammonium bromide began to crystallise out. After twenty-four hours the alcoholic ammonia solution was separated from the crystals of ammonium bromide, and the alcohol and unchanged ethyl bromide were distilled off. Water was added to the residue and the last traces of alcohol were removed by boiling. The hydrobromides of the mixed bases were then decomposed by a very concentrated solution of sodium hydroxide and the liberated amines distilled off. The alcoholic ammonia containing the ethyl bromide was used again for the preparation of more of the mixed hydrobromides. By using a fractionating column with ten bulbs there

is no difficulty in obtaining an effective separation of the bases. The yields were:

	Per cent.
Monoethylamine	10·9
Diethylamine	17·9
Triethylamine	19·1

About 80 per cent. of the diethylamine (boiling within 1°) can be obtained by two fractional distillations. A further quantity of the mixed bases can be produced from the monoethylamine by treating it with more ethyl bromide.

Five hundred grams of crude monoethylamine (containing about 10 per cent. of diethylamine) were dissolved in 2500 c.c. of alcohol and 1000 grams of ethyl bromide were added. The mixture must be cooled in ice, since much heat is evolved. After twenty-four hours 200 grams of ammonium bromide were added to fix any free bases, and the solution was treated as described above. The yields were:

	Per cent.
Monoethylamine	38·7
Diethylamine	30·1
Triethylamine	17·3
	86·1

As the monoethylamine can be again used for the preparation of diethylamine, about 50 per cent. of the monoethylamine can be converted into diethylamine.

The authors are much indebted to Prof. Collie for the interest he has taken in the above work.

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LONDON.

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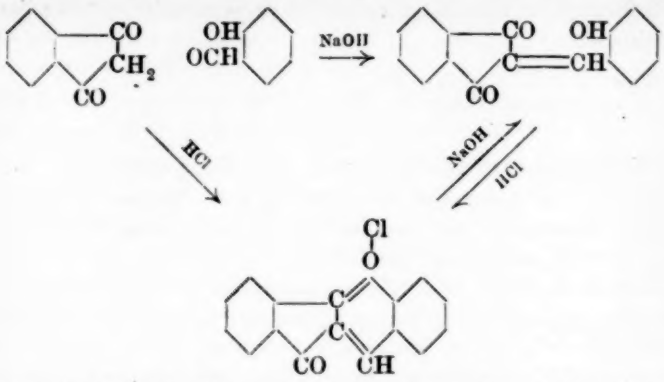
XIX.—*Synthesis of Ketoindopyranols.*

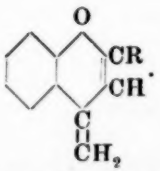
By SOSALE GARALAPURY SASTRY and BROJENDRA NATH GHOSH.

IN an investigation on the properties of diketohydrindene we were able to show in an earlier paper (T., 1915, **107**, 1442) that aromatic *o*-hydroxyaldehydes condense with diketohydrindene in the presence of alkali, giving unsaturated ketonic compounds which in the presence of dry hydrogen chloride are converted into ketoindopyran hydrochlorides. The reactions involved may be represented as follows:

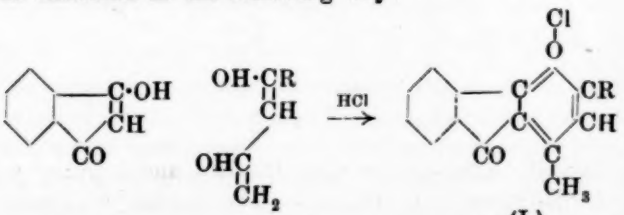


It appeared that diketones of the type of acetylacetone and benzoylacetone might be able to react in a similar way. However, on attempting to condense diketohydrindene with acetylacetone in the presence of alkali, the reaction did not take place, but when dry hydrogen chloride was passed into a mixture of the two substances, dissolved in a solvent, a condensation product was obtained which is probably a derivative of ketoindopyranol.

It has been proved by Bülow and others (Bülow and Wagner, *Ber.*, 1901, **34**, 1189; Bülow, *ibid.*, 1903, **36**, 190; Bülow and Deiglmayr, *ibid.*, 1904, **37**, 1791; Decker and Becker, *ibid.*, 1914, **47**, 2288; Collie and White, T., 1915, **107**, 369; Ghosh, T., 1915, **107**, 739) that phenols react with diketones to give pyranol derivatives of the type



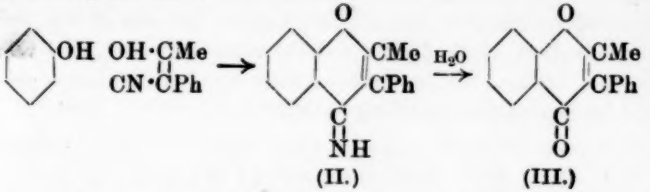
In the present case it may well be that diketohydrindene enolises in the presence of hydrogen chloride, and is then capable of reacting with diketones in the following way:



(I.)

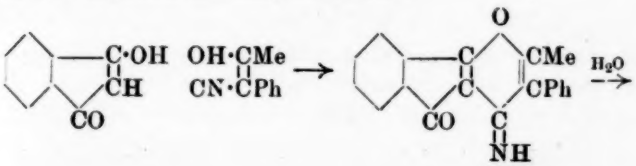
It has been shown by one of us that ketonitriles, such as acetylphenylacetonitrile, react with phenols in the following manner,

giving iminopyranol derivatives, which on hydrolysis give the corresponding flavones:

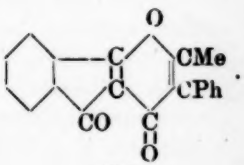


(II.) (III.)

It was thought that diketohydrindene might also react in a similar way, and experiments showed that the reaction proceeded in the expected manner, as follows:



(IV.)

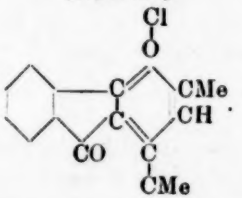


(V.)

The substances are all deeply coloured, and the arguments set forth in our earlier paper (*loc. cit.*) with regard to their constitution apply also in the present instance.

EXPERIMENTAL.

4'-Keto-4-methylene-6-methyl-2:3-indenopyran(1:4) *Hydrochloride*,

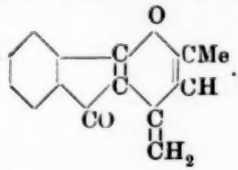


A mixture of 7 grams of diketohydrindene and 5 grams of acetyl acetone was dissolved in a small quantity of methyl alcohol, and a rapid current of dry hydrogen chloride was passed through the solution for four to five hours. The solution became dark red and

was set aside. After three days a crystalline compound began to separate out. The solution was saturated from time to time with dry hydrogen chloride, and the crystalline compound was collected after seven days, washed with a little methyl alcohol, and recrystallised from dilute acetic acid containing hydrochloric acid. It formed brown needles melting at 120°:

0·1080 gave 0·2700 CO_2 and 0·0442 H_2O. C = 68·17; H = 4·54.
$C_{14}H_{10}O_2$,HCl requires C = 68·15; H = 4·44 per cent.

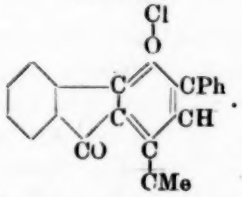
4′-Keto-6-methyl-4-methylene-2:3-indenopyran(1:4),



This was prepared by dissolving the corresponding hydrochloride in alcohol and treating the solution with an excess of aqueous sodium acetate; the precipitate was collected and crystallised from alcohol, separating in brown prisms melting at 182°. It is readily soluble in benzene or acetic acid, but sparingly so in alcohol. In concentrated sulphuric acid it dissolves to a dark red solution. It is insoluble in cold sodium hydroxide solution, but dissolves readily on heating to a purple solution:

0·1410 gave 0·4120 CO_2 and 0·0660 H_2O. C = 79·64; H = 5·20.
$C_{14}H_{10}O_2$ requires C = 80·00; H = 5·02 per cent.

4′-Keto-6-phenyl-4-methylene-2:3-indenopyran(1:4) *Hydrochloride*,



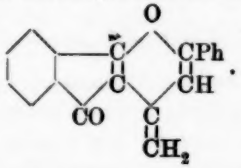
A mixture of 3·5 grams of diketohydrindene and 4 grams of benzoylacetone was dissolved in a small quantity of glacial acetic acid, and the solution was saturated with dry hydrogen chloride, when a crystalline compound slowly separated out. The mixture was kept for thirty-six hours and then filtered; the precipitate was washed with acetic acid and crystallised from the same solvent containing a little hydrochloric acid, when there were obtained

brown prisms melting at 190—200°. The substance is almost insoluble in alcohol, but readily soluble in pyridine or acetic acid:

0·1342 gave 0·3604 CO_2 and 0·0480 H_2O. C = 74·00; H = 3·97.

$C_{19}H_{12}O_2$,HCl requires C = 74·00; H = 4·12 per cent.

4′-Keto-6-phenyl-4-methylene-2:3-indenopyran(1:4),

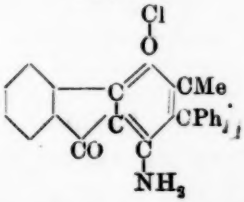


This was prepared by dissolving the corresponding hydrochloride in a small quantity of pyridine and precipitating the free base by the addition of water. The precipitate was collected, washed with water, and recrystallised from hot dilute pyridine, when it separated in brown prisms melting and decomposing at 219°:

0·1136 gave 0·3488 CO_2 and 0·0480 H_2O. C = 83·73; H = 4·69.

$C_{19}H_{12}O_2$ requires C = 83·82; H = 4·41 per cent.

4-Imino-4′-keto-5-phenyl-6-methyl-2:3-indenopyran(1:4) *Hydrochloride*,



This was prepared by passing a current of dry hydrogen chloride into a cold mixture of 3·5 grams of diketohydrindene and 4 grams of acetylphenylacetonitrile dissolved in glacial acetic acid. The crystals that separated were collected after twenty-four hours and washed with a little glacial acetic acid, and recrystallised from the same solvent containing a little hydrochloric acid. Dark red needles were obtained, which melted and decomposed at 210°:

0·1204 gave 0·3106 CO_2 and 0·0476 H_2O. C = 70·34; H = 4·39.

$C_{19}H_{13}O_2N$,HCl requires C = 70·58; H = 4·32 per cent.

4-Imino-4′-keto-5-phenyl-6-methyl-2:3-indenopyran(1:4) (IV).

The free base was prepared in the usual manner by treating an alcoholic solution of the hydrochloride with an excess of aqueous sodium acetate. It crystallises from dilute alcohol in brown prisms

melting and decomposing at 222°. It dissolves in concentrated sulphuric acid, giving a dark red solution. On boiling with dilute sodium hydroxide, it gradually dissolves to a red solution, with the evolution of ammonia:

0·1070 gave 0·3120 CO_2 and 0·0422 H_2O. C = 79·52; H = 4·38.
$C_{19}H_{13}O_2N$ requires C = 79·44; H = 4·53 per cent.

4 : 4′-Diketo-5-phenyl-6-methyl-2 : 3-indenopyran(1 : 4) (V).

This was prepared by boiling 3 grams of 4-imino-4′-keto-5-phenyl-6-methyl-2 : 3-indenopyran(1 : 4) hydrochloride with 30 c.c. of 10 per cent. sulphuric acid for four to five hours. The precipitate was collected, washed with water, and crystallised from dilute alcohol, when it was obtained in pale yellow needles melting at 256°. It is sparingly soluble in benzene, but readily so in alcohol or acetic acid. On boiling with dilute alkali hydroxide it dissolves to a dark red solution:

0·1114 gave 0·3230 CO_2 and 0·0444 H_2O. C = 79·07; H = 4·42.
$C_{19}H_{12}O_3$ requires C = 79·16; H = 4·16 per cent.

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XX.—*Decompositions of Sodium Diacetamide and Potassium Acetamide.*

By JITENDRA NATH RAKSHIT.

THIS investigation was undertaken in order to ascertain whether the metal in the sodium or potassium acid amides is linked to the basic nitrogen or to the acidic oxygen. Titherley (T., 1897, **71**, 461; 1901, **79**, 391) has made several experiments to determine the position of the metal in such compounds. For the purpose in view it was thought useful to observe the behaviour of these amides towards alcohol and water, and the ultimate transformation of the metals when such compounds are decomposed by heat. On heating sodium diacetamide (T., 1913, **103**, 1559) sodium carbonate was left as a residue, and a mixture of acetonitrile and acetone was distilled off:

$$2C_4H_6O_2NNa = Na_2CO_3 + 2CH_3{\cdot}CN + CH_3{\cdot}CO{\cdot}CH_3.$$

As the residue was found to be pure sodium carbonate quite free from cyanide, the equation completely represents the reaction. It

may be concluded from the formation of sodium carbonate that the constitution of sodium diacetamide is $CH_3 \cdot CO \cdot N{:}C(ONa) \cdot CH_3$. Even if the compound did not possess this constitution originally it would be expected to pass through this form before decomposing into the above products.

When potassium acetamide is similarly heated, potassium hydroxide and acetonitrile are formed:

$$CH_3 \cdot CO \cdot NHK = KOH + CH_3 \cdot CN.$$

In this case, however, the equation does not strictly represent the reaction, because potassium cyanide, ammonia, an insoluble oil, and a gas are formed simultaneously.

Reactions with Alcohol.

Since Titherley (*loc. cit.*, p. 467) has noted that sodium acetamide is stable in alcohol it was thought that it might be prepared by the interaction of sodium ethoxide and acetamide in alcoholic solution. Accordingly, calculated quantities of 2*N*-solution of sodium ethoxide and acetamide were mixed, and kept in a vacuum desiccator over sulphuric acid. When dry, the residue was found to be sodium acetate, and the sulphuric acid contained only ammonia. Hence the acetamide underwent the usual hydrolysis to acetic acid and ammonia, abstracting, in the process, 1 molecule of water from alcohol, the latter being transformed into ether in the presence of the strong alkali, sodium ethoxide (compare Scott, T., 1909, **95**, 1200; Rây and Rakshit, T., 1912, **101**, 217).

When 0·403 gram of sodium diacetamide was dissolved in the minimum quantity of absolute alcohol and kept in a vacuum desiccator over sulphuric acid, it dried in four days, but no loss or gain of weight was observed. On adding an alcoholic solution of sodium diacetamide to a 60 per cent. alcoholic solution of silver nitrate, a brown precipitate was immediately formed, which turned black in a few minutes, but when the silver nitrate solution was added drop by drop to the other solution a pale orange precipitate was formed, which disappeared on shaking, being soluble in excess of sodium diacetamide. On adding more silver nitrate solution to it, the brown precipitate became permanent, and blackened with the usual rapidity.

Decomposition with Water.

In a platinum basin 0·760 gram of sodium diacetamide was dissolved in a minimum quantity of water. No odour of ammonia was observed. The solution was kept in a vacuum desiccator over sulphuric acid, when in about two hours white crystals of ammon-

ium sulphate became visible on the inside of the desiccator, and on removing the lid a very strong odour of ammonia was noticed. The residue in the basin attained to constant weight after three days, namely, 0·819 gram, an increase in weight of 7·75 per cent. The residue was repeatedly extracted with hot benzene, and the insoluble portion was proved to be sodium acetate. The benzene extract was evaporated, and the residue, after being twice recrystallised from benzene, proved to be diacetamide (Found, N = 13·4. Calc., N = 13·8 per cent.). This hydrolytic decomposition must have taken place according to the following equations:

$$(CH_3\cdot CO)_2NNa + H_2O = CH_3\cdot CO_2Na + CH_3\cdot CO\cdot NH_2.$$
$$CH_3\cdot CO\cdot NH_2 + (CH_3\cdot CO)_2NNa + H_2O = CH_3\cdot CO_2Na + (CH_3\cdot CO)_2NH + NH_3.$$

Or:

$$(CH_3\cdot CO)_2NNa + 2H_2O = CH_3\cdot CO_2Na + CH_3\cdot CO_2NH_4.$$
$$(CH_3\cdot CO)_2NNa + CH_3\cdot CO_2NH_4 = (CH_3\cdot CO)_2NH + NH_3 + CH_3\cdot CO_2Na.$$

According to either set of equations the increase in weight should be 7·72 per cent. Potassium acetamide also underwent a similar decomposition into acetic acid and ammonia when treated in the same manner.

Decomposition of Sodium Diacetamide by Heat.

In order to study the decomposition of sodium diacetamide by heat a large quantity of the compound was prepared by the method previously described (*loc. cit.*). It may be mentioned that in order to avoid much contamination of the derivative with unchanged acetamide it was convenient to filter when ebullition had just ceased, instead of allowing the liquid to cool. After being dried, the products of different preparations were stored in a stoppered bottle, and each time this was opened a distinct odour of ammonia was perceived. During transference the substance rapidly absorbed moisture, which subsequently led to the evolution of ammonia, according to the equations already given.

Sixty-three grams of sodium diacetamide were heated in a distilling flask connected with a condenser. At first the compound began to melt and to decompose, with the evolution of a vapour which condensed as a colourless liquid. Almost the whole of this liquid was collected up to 80°. As the rate of the collection of the liquid gradually diminished, the contents of the flask were more strongly heated. The thermometer rapidly rose to 210°, and then slowly to 215°, but very little liquid passed over. As the decomposition of the molten mass completed, it gradually solidified. A slightly

black solid was left in the flask, which was shown to be sodium carbonate mixed with 0·2 gram of carbon. Sometimes towards the end of the experiment, especially when the substance was old, a small amount of a brown liquid distilled over at 210—218° and solidified in the condenser. This was found to be acetamide or diacetamide or a mixture of the two. In one case when it was dried in a vacuum over sulphuric acid it melted at 80·5° and gave C = 42·1, H = 8·6, whereas acetamide requires C = 40·7, H = 8·4 per cent. In another case it gave N = 20·07, whereas acetamide and diacetamide require N = 23·28 and 13·59 per cent. respectively.

The crude distillate of the above experiment (17·8 grams) was dried over anhydrous potassium carbonate and then distilled, when 10·5 grams passed over at 68—80°, after which the thermometer constantly indicated 84° for about half an hour, but no liquid distilled. On further heating the thermometer rose to 215°, and a very small quantity of liquid distilled over, which soon solidified to a transparent, crystalline mass. On crystallisation from benzene it gave N = 18·03 per cent., showing it to be a mixture of acetamide and diacetamide.

The liquid collected at 68—80° could not be separated by fractional distillation into its components, and therefore two fractions were collected, at 70—72° and 73—80° respectively.

The first fraction gave C = 59·90, 59·90; H = 8·40, 8·86; N = 17·96, 17·04 per cent., and was proved to consist of a mixture of acetone and acetonitrile. In estimating acetone by Messenger's method, 0·1285 required 62·7 c.c. *N*/10-iodine, whence the percentage of acetone in the sample is 47·19. Now if the remaining 52·81 per cent. is acetonitrile, then the percentage of carbon, hydrogen, and nitrogen in the mixture is 59·83, 8·70, and 17·81 respectively. These numbers agree fairly well with the result obtained by analysis.

The second fraction gave C = 59·02; H = 7·72; N = 28·67, 28·16 per cent., and also responded to qualitative tests for acetone and acetonitrile. In the estimation of acetone, 0·2464 required 41·6 c.c. *N*/10-iodine, which is equivalent to 16·34 per cent. of acetone. Assuming the remaining 83·66 per cent. to be acetonitrile, the percentages of carbon, hydrogen, and nitrogen become 59·01, 7·80, and 28·51 respectively, which also agree with the above results.

Decomposition of Potassium Acetamide by Heat.

Seventy-two grams of potassium acetamide were heated in a similar manner to the sodium compound. The substance first melted and then solidified, giving a colourless liquid and a gas. The gas, which had the odour of ammonia, was passed through dilute hydrochloric acid, but a small quantity was always found

to escape absorption in the acid. The hydrochloric acid solution was evaporated, and was found to contain only ammonium chloride. The residue in the flask was potassium hydroxide mixed with potassium cyanide and a small quantity of carbonate. In this case also there was some charring, but the quantity of carbon formed was less than in the case of sodium diacetamide. The total liquid collected was 10·0 c.c., and weighed 9·0 grams. After being dried it was distilled, when two fractions were collected, the first boiling at 72—73° and the second at 73—82°. The former was proved to consist of a mixture of acetone and acetonitrile, the amount of acetone being 10·11 per cent. The formation of acetone during the reaction is due to the decomposition of potassium acetate formed by the hydrolysis of the compound through the unavoidable absorption of moisture from the air owing to its extremely hygroscopic nature. This explanation is also supported by the observation that when a bottle of the substance was left open for some time it evolved a strong odour of ammonia. The decomposition of potassium acetate would result in the formation of potassium carbonate, which has already been stated to be a constituent of the residue.

The second fraction was similar in appearance and odour to the first one, but it did not dissolve completely in water, always leaving a small quantity of an oil floating on the top. It was also shown to consist of a mixture of acetonitrile and acetone, the quantity of the latter being 4·62 per cent. The small quantity of oil just mentioned was not further examined.

I wish to express my best thanks to the Research Fund Committee of the Chemical Society for a grant, which has partly defrayed the cost of this investigation.

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[*Received, September 30th*, 1915.]

XXI.—*The Estimation of Mixtures of Paracetaldehyde and Acetal.*

By KENNEDY JOSEPH PREVITÉ ORTON and PHYLLIS VIOLET MCKIE.

A SIMPLE and fairly accurate means of estimating mixtures of paracetaldehyde and acetal can be based on the different rates with which each is decomposed in the presence of dilute aqueous acids. Paracetaldehyde is converted into acetaldehyde, whilst the acetal is

hydrolysed into alcohol and acetaldehyde. The acetaldehyde is distilled off and determined by one of the standard methods. The procedure is well adapted for estimating acetal and paracetaldehyde either alone or together or mixed with acetaldehyde in the usual neutral media.

Whilst acetal is not hydrolysed, or hydrolysed very slowly, in neutral or alkaline aqueous solutions, hydrolysis is very rapid in the presence of traces of strong acids. At such small concentrations, on the other hand, no decomposition of paracetaldehyde can be detected. Thus a 1 per cent. solution of acetal in an $N/6000$-solution of a strong acid, or of any acid solution in which the hydrion is at that concentration, is completely hydrolysed after a few minutes' boiling. When a similar aqueous acid solution of paracetaldehyde is distilled, no acetaldehyde can be detected in the distillate until the concentration of the hydrion has risen to $N/2000$. Moreover, it is only in solutions of $N/10$—$N/7{\cdot}5$ of a strong acid that the conversion to acetaldehyde attains a speed comparable to that of the hydrolysis of acetal in the highly dilute acid.

For the analysis, 0·2 to 0·4 gram of the mixture is added to 30 c.c. of dilute acid of the required concentration in a small flask of the Kjeldahl type, which is fitted to an efficient condenser. The distillate is collected in a receiver (for example, a small measuring cylinder) attached to the condenser by means of an adapter. The receiver is well cooled, and should contain about 10 c.c. of water or alcohol for the better absorption of the acetaldehyde. The mixture is gently heated and 7 c.c. distil over when acetal, or 10 c.c. when paracetaldehyde, is being determined.

In the estimation of acetal, the hydrion is at a concentration of $N/5000$. For such small quantities (0·000219 gram, for example, of hydrochloric acid) it is better to use a weak acid; the right concentration of hydrion is given by diluting 7 c.c. of $N/100$-acetic acid to 30 c.c.

For determining paracetaldehyde (or the total acetal and paracetaldehyde in a mixture) 30 c.c. of $N/5$-hydrochloric acid are used.

The acetaldehyde can be determined in the distillate either by the hydrogen sulphite (Ripper's modification, *Monatsh.*, 1900, **21**, 1079) or by the neutral sulphite method (Seyewetz, *Bull. Soc. Chim.*, 1905, [iii], **33**, 1000). Both methods give quite concordant results. The neutral sulphite requires more practice but less time. Feinberg (*Amer. Chem. J.*, 1913, **49**, 97) takes objection to the delicacy of the latter method, but we find that Seyewetz's claims are fully substantiated in the case of acetaldehyde.

It is obvious that mixtures of acetaldehyde, acetal, and paracet-

aldehyde can be analysed by determining (*a*) the acetaldehyde, (*b*) acetal and acetaldehyde, (*c*) acetaldehyde, acetal, and paracetaldehyde.

The following analyses are typical, using Seyewetz's method for estimating the acetaldehyde:

	I.	II.	III.	IV.
Acetal used	0·0835	0·1336	0·1837	0·2255
Paracetaldehyde used	0·883	0·4316	0·0784	0·0294
C.c. of 0·099*N*-H_2SO_4 for acetal	7·1	12·1	16·6	18·8
C.c. of 0·099*N*-H_2SO_4 for acetal and paracetaldehyde	200·0	108·7	32·0	25·0
Acetal found	0·0835	0·1337	0·1837	0·2277
Paracetaldehyde found	0·889	0·43	0·0764	0·031

An alcoholic solution made up to contain 1·67 grams of acetal and 1·964 grams of paracetaldehyde in 100 c.c. gave on analysis 1·664 grams of acetal and 1·960 grams of paracetaldehyde.

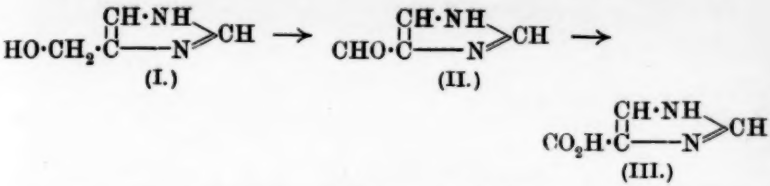
UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR. [*Received, February 9th*, 1916.]

XXII.—*Derivatives of Glyoxaline-4(or 5)-formaldehyde and Glyoxaline-4(or 5)-carboxylic Acid. A New Synthesis of Histidine.*

By FRANK LEE PYMAN.

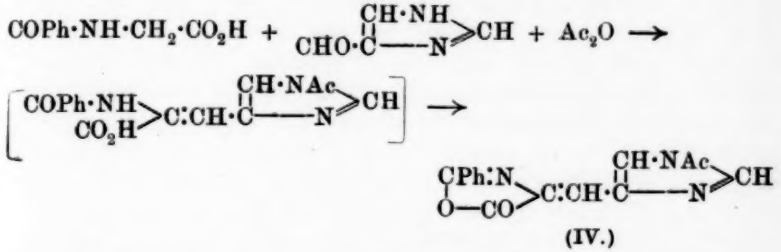
SOME of the simpler substituted glyoxalines are little known. The simplest aldehyde in this field, glyoxaline-4(or 5)-formaldehyde (II), was obtained by the author (T., 1912, **101**, 542) in a yield of 15 per cent. of the theoretical by the oxidation of 4(or 5)-hydroxymethylglyoxaline (I) by means of chromic acid. As the analogue of benzaldehyde, the starting material for many syntheses in the aromatic series, this substance is of some importance. Its preparation and some of its reactions have therefore been studied.

Glyoxalineformaldehyde may be obtained in a yield of more than 50 per cent. of the theoretical by the oxidation of hydroxymethylglyoxaline with little more than the calculated quantity of nitric acid, and its stability towards oxidising agents is such that it is obtained in a small yield, together with large quantities of glyoxaline-4(or 5)-carboxylic acid (III), when the alcohol is oxidised with a very large excess of nitric acid over the quantity required for its conversion into the acid.



(I.) (II.) (III.)

Glyoxalineformaldehyde yields a *phenylhydrazone*, and a *cyanohydrin* which will be discussed later. It does not undergo Perkin's reaction for the synthesis of the acrylic acid in a satisfactory manner, decomposition taking place. On the other hand, it can be condensed very easily with hippuric acid by means of acetic anhydride and sodium acetate, yielding 2-*phenyl*-4-[1-*acetylglyoxaline*-4(or 5)-*methylidene*]-*oxazolone* (IV).



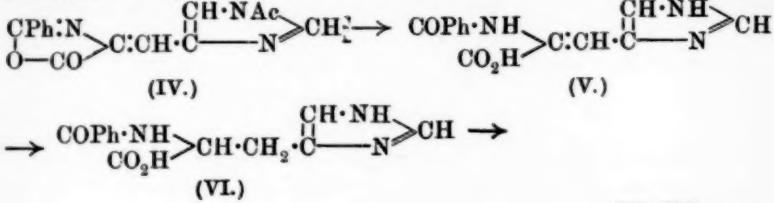
(IV.)

This condensation has made it possible to effect a synthesis of histidine on the lines of the synthesis of phenylalanine carried out by Plöchl (*Ber.*, 1884, **17**, 1616) and Erlenmeyer, jun. (*Annalen*, 1893, **275**, 1), and that of tyrosine due to Erlenmeyer, jun., and Halsey (*Annalen*, 1899, **307**, 138).

The oxazolone (IV) is obtained in a yield of 68 to 76 per cent. of the theoretical. The acetyl group which it contains doubtless replaces the imiño-hydrogen atom of the glyoxaline ring, for it is easily removed on hydrolysis, and there is, indeed, no other possible point of attachment. The formation of isomeric 1:4- and 1:5-acetyl derivatives would be expected on acetylation of a 4(or 5)-substituted glyoxaline, analogous to the formation of 1:4- and 1:5-dimethylglyoxaline on the methylation of 4(or 5)-methylglyoxaline (T., 1910, **97**, 1814), but the above described compound is homogeneous. In this connexion it may be noted that Gerngross (*Ber.*, 1913, **46**, 1908) has prepared the *N*-benzoyl derivatives of several 4(or 5)-substituted glyoxalines, and does not record the formation of isomerides in any case.

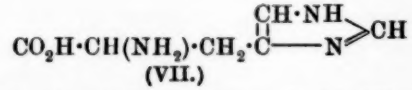
When the oxazolone is boiled with very dilute aqueous sodium carbonate, the acetyl group is removed and the oxazolone ring is opened. On then mixing the solution with the calculated quantity

of an acid, *α-benzoylamino-β-glyoxaline-4(or 5)-acrylic acid* (V) is precipitated.



(IV.) (V.)

(VI.)



(VII.)

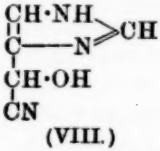
The reduction of this acid to the saturated acid, *benzoyl-r-histidine* (VI), and hydrolysis of the latter to *r*-histidine (VII), were carried out according to E. Fischer's modifications (*Ber.*, 1899, **32**, 3638) of Erlenmeyer, jun.'s, methods for the treatment of the corresponding acids in the synthesis of tyrosine. Benzoyl-*r*-histidine has not been prepared previously. It crystallises from water with one molecular proportion of the solvent, and melts and decomposes at 248° (corr.) In both these respects it resembles benzoylhistidine, which also crystallises with $1H_2O$ according to Fränkel (*Beitr. chem. Physiol. Path.*, 1906, **8**, 156), who gives the melting point as 230°; Pauly, however (*Ber.*, 1910, **43**, 2254), states that it melts at 249° (corr.). The identity of *r*-histidine prepared by the above method was proved by comparison with a specimen previously synthesised by another method (T., 1911, **99**, 1386).

It has been stated above that glyoxalineformaldehyde yields a cyanohydrin (VIII). This compound is very unstable and readily loses hydrogen cyanide, regenerating the starting material. In a cold solution, however, it can be reduced by means of sodium amalgam and hydrochloric acid in nearly neutral solution (compare Meister, Lucius, & Brüning, D.R.-P. 193634 *) to give *β-hydroxy-*

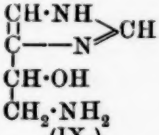
* Mannich and Thiele (*Arch. Pharm.*, 1915, **253**, 181) have recently described a method for the preparation of β-hydroxy-β-arylethylamines by the reduction of phenyl aminomethyl ketones with hydrogen in the presence of palladinised charcoal.

In discussing previous methods, they dismiss the method of D.R.-P. 193634 with the remark that it does not seem to be of practical importance, and they also overlook the fact that this patent describes the preparation of phenylethanolamine (β-hydroxy-β-phenylethylamine), which they claim to have prepared for the first time. As a matter of fact, this substance is described in the patent and can be prepared easily and quickly from benzaldehyde, as there stated, in a yield of more than 30 per cent. of the theoretical, whereas Mannich and Thiele's method involves the previous preparation of ω-aminoacetophenone (Mannich and Hahn, *Ber.*, 1911, **44**, 1542), for which ω-bromoacetophenone is required.

β-glyoxaline-4(or 5)-*ethylamine* (IX) in a yield amounting to 32 per cent. of the theoretical, calculated on the glyoxalineformaldehyde.



(VIII.)



(IX.)

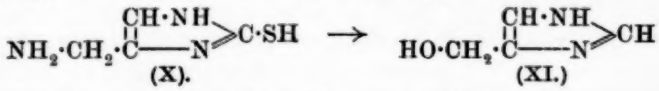
The new base was prepared in order to compare its physiological action with that of 4(or 5)-β-aminoethylglyoxaline, a base which occurs in extracts of ergot (Barger and Dale, T., 1910, **97**, 2592), and is of great physiological activity (Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318). Constitutionally, it differs from the latter only in containing a hydroxyl group, so that in the place of the ethylamine group it contains an ethanolamine group similar to that contained in adrenaline, the active principle of the suprarenal glands. The comparison of the ethylamine and ethanolamine derivatives of glyoxaline was interesting, because Barger and Dale (*J. Physiol.*, 1910, **41**, 19) have compared previously the ethylamine and ethanolamine derivatives of phenols. They showed that β-hydroxy-β-*p*-hydroxyphenylethylamine was inferior in its sympathomimetic action to β-*p*-hydroxyphenylethylamine, having only one-fifth of the power, whilst β-hydroxy-β-3:4-dihydroxyphenylethylamine is fifty times as powerful as β-3:4-dihydroxyphenylethylamine. In the present case, experiments kindly carried out by Dr. H. H. Dale, F.R.S., have shown that the introduction of the hydroxyl group has diminished the physiological activity, β-hydroxy-β-glyoxaline-4(or 5)-ethylamine being less active than 4(or 5)-β-aminoethylglyoxaline.

In the course of this work a considerable amount of glyoxaline-4(or 5)-carboxylic acid (III) was accumulated, and the opportunity was taken of studying its properties. This acid was first described by Knoop (*Beitr. chem. Physiol. Path.*, 1907, **10**, 111), who obtained it by the oxidation of glyoxaline-4(or 5)-glyoxylic acid, an oxidation product of histidine. Knoop stated that he had also prepared it synthetically from glyoxaline-4:5-dicarboxylic acid, which can be prepared from tartaric acid, and that the synthesis was to be described in another place. No further account of the work seems to have appeared. Windaus and Ullrich (*Zeitsch. physiol. Chem.*, 1914, **90**, 366) subsequently isolated the acid from the products of reaction of dextrose and ammoniacal copper hydroxide. Both authors agree that the acid melts and effervesces at about 286°, losing carbon dioxide and yielding glyoxaline.

Several salts of glyoxalinecarboxylic acid with acids have now

been prepared, and also the *methyl* and *ethyl esters*. The esters behave in an abnormal manner towards sodium diazobenzene-*p*-sulphonate. Glyoxalines containing a free imino-hydrogen atom couple with this reagent in aqueous sodium carbonate, forming a carmine-coloured solution; glyoxalinecarboxylic acid itself behaves normally, but the esters fail to give a red colour. Gerngross (*Ber.*, 1912, **45**, 513) has previously noticed the same phenomenon with 5(or 4)-methylglyoxaline-4(or 5)-carboxylic acid and its esters; here also the acid couples, but the esters do not. Attempts to prepare the acid chloride of glyoxalinecarboxylic acid hydrochloride have so far proved quite unsuccessful, for the acid fails to react with thionyl chloride or with phosphorus pentachloride, either alone or when mixed with other acid chlorides even at high temperatures. In this connexion it is of interest to note that H. Meyer (*Monatsh.*, 1901, **22**, 415) found that whilst *o*- and *m*-hydroxybenzoic acids were readily converted into the acid chlorides by means of thionyl chloride, the para-isomeride remained unaltered.

In the course of purifying a quantity of hydroxymethylglyoxaline (XI), prepared by the action of nitric acid on 2-thiol-4(or 5)-aminomethylglyoxaline (X) (T., 1911, **99**, 669), a by-product * having

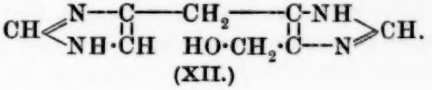


(X). (XI.)

the empirical formula $C_8H_{10}ON_4$ was isolated. This compound can be coupled with sodium diazobenzene-*p*-sulphonate, giving a red dye, a characteristic of glyoxaline derivatives. It is a diacidic base forming well-crystallised neutral salts. Taking into account its mode of formation and properties, there can be little doubt that it contains two glyoxalinemethyl groups ($C_3H_3N_2 \cdot CH_2 \cdot$), which account for all the elements it contains except the one oxygen atom. It thus appeared that the substance was either glyoxalinemethyl ether, $(C_3H_3N_2 \cdot CH_2)_2O$, or glyoxalinemethyl-glyoxalinemethyl alcohol, $C_3H_3N_2 \cdot CH_2 \cdot C_3H_2N_2 \cdot CH_2 \cdot OH$. In order to determine which formula was correct, the substance was heated under pressure with acids, when it was found to be unchanged. It did not therefore appear to be an ether. It was consequently presumed to have the alternative alcohol formula, and this view was shown to be correct in the following manner. The substance was heated with benzoyl chloride on the water-bath, when a *monobenzoyl* derivative, $C_{15}H_{14}O_2N_4$, was obtained. The same method had been employed previously for the benzoylation

* The occurrence of this base as a by-product in the preparation of hydroxymethylglyoxaline was discovered by Mr. W. H. Taylor, B.Sc., who kindly drew the author's attention to it.

of hydroxymethylglyoxaline, $C_3H_3N_2 \cdot CH_2 \cdot OH$ (T., 1912, **101**, 541), when glyoxalinemethyl benzoate, $C_3H_3N_2 \cdot CH_2 \cdot O \cdot COPh$, was obtained. The method did not, therefore, lead to the formation of an *N*-benzoylglyoxaline derivative. Such compounds are only obtained under special conditions, and are unstable in moist air (Gerngross, *Ber.*, 1913, **46**, 1908). The benzoyl derivative, $C_{15}H_{14}O_2N_2$, is stable, and can be recrystallised from water without decomposition. These facts show that the benzoyl derivative is not a *N*-benzoyl, but an *O*-benzoylglyoxaline derivative, and indicate that it is glyoxalinemethylglyoxalinemethyl benzoate. The formation of glyoxalinemethylglyoxalinemethyl alcohol is due to the displacement of one of the hydrogen atoms of hydroxymethylglyoxaline by the glyoxalinemethyl group. Now, the condensation of 4(or 5)-methylglyoxaline with formaldehyde leads to 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline, the substituent taking up the 5(or 4)-position (Windaus, *Ber.*, 1909, **42**, 758; Ewins, T., 1911, **99**, 2052), and it seems probable that in the present case also the substituent group occupies the corresponding position. The substance is thus in all probability 4(or 5)-[*glyoxaline*-4(or 5)-*methyl*]-*glyoxaline*-5(or 4)-*methyl alcohol* (XII):



(XII.)

EXPERIMENTAL.

Oxidation of 4(or 5)-*Hydroxymethylglyoxaline.*

Hydroxymethylglyoxaline is readily oxidised by means of concentrated nitric acid, giving a mixture of glyoxalineformaldehyde and glyoxalinecarboxylic acid. The relative amounts of each of these substances obtained depend on the proportion of nitric acid employed, and methods have been worked out for preparing both compounds in good yield.

(*a*) *Preparation of Glyoxalineformaldehyde.*—Twenty-six grams of hydroxymethylglyoxaline and 38 c.c. of nitric acid (D 1·42) were digested in a covered dish on the water-bath until the evolution of brown fumes was almost complete. The cover was then removed and the liquid evaporated, when a crystalline mass remained. This was dissolved in a warm concentrated solution of sodium carbonate and kept, when 11·3 grams of glyoxalineformaldehyde (m. p. 170°) crystallised. After removing the crystals, the filtrate was acidified faintly to methyl-orange with hydrochloric acid and kept, when 5·1 grams of glyoxalinecarboxylic acid separated. This was collected and the filtrate evaporated nearly to dryness. The

residue was mixed with alcohol, filtered from inorganic salts, and evaporated to remove the alcohol. This residue was dissolved in warm concentrated aqueous sodium carbonate and kept, when 3·1 grams of glyoxalineformaldehyde (m. p. 170°) crystallised. The yields of the aldehyde and the acid are 56 and 17 per cent. of the theoretical respectively.

(*b*) *Preparation of Glyoxalinecarboxylic Acid.*—Seventeen grams of hydroxymethylglyoxaline were dissolved in 100 c.c. of concentrated nitric acid (three times the quantity calculated for its conversion into the nitrate of glyoxalinecarboxylic acid) and warmed on the water-bath in a covered dish until the evolution of brown fumes was almost complete. The liquor was then evaporated to dryness on the water-bath and the crystalline residue dissolved in water. A sufficient quantity (about 45 c.c.) of a cold saturated aqueous solution of sodium carbonate was added until the liquor was only slightly acid to methyl-orange. This caused the separation of the bulk of the glyoxalinecarboxylic acid (10·6 grams) as a colourless, crystalline powder which melted and decomposed at 281°. After the removal of this crop, the filtrate and washings were evaporated to a small volume and treated with sodium carbonate until neutral to methyl-orange, a further crop of 3·0 grams of glyoxalinecarboxylic acid (m. p. 275°) being thus obtained. The mother liquor was added to a solution of 12 grams of picric acid in 300 c.c. of boiling water, and after keeping overnight 6·4 grams of glyoxalineformaldehyde picrate (m. p. 191°) separated. The mother liquor was concentrated to half volume and kept, when glyoxalinecarboxylic acid picrate crystallised out mixed with a little picric acid and sodium picrate. It was purified by recrystallisation from water, when 5·0 grams of the pure salt were obtained.

The total yields represent 15·3 grams of glyoxalinecarboxylic acid and 1·9 grams of glyoxalineformaldehyde, that is, 82 and 11 per cent. of the theoretical respectively.

(*c*) An oxidation was also carried out with a quantity of nitric acid only slightly greater (using 3·5 instead of 3·0 molecular proportions) than that calculated for the conversion of hydroxymethylglyoxaline into glyoxalinecarboxylic acid nitrate. In this case the yields of acid and aldehyde were 55 and 29 per cent. of the theoretical respectively.

*Glyoxaline-4(or 5)-formaldehyde,** $C_3H_3N_2 \cdot CHO$.

This base and its acid oxalate and picrate were described briefly in a previous paper (T., 1912, **101**, 542). Glyoxalineformaldehyde is not easily oxidisable; it is stable in the air and does not reduce ammoniacal silver nitrate. Its aqueous solution gives with this reagent a white precipitate like that of other glyoxalines containing a free imino-group, but this precipitate remains unchanged when the ammoniacal silver nitrate in which it is suspended is boiled. Glyoxalineformaldehyde gives a red dye with sodium diazobenzene-*p*-sulphonate. An attempt to convert glyoxalineformaldehyde into glyoxalineacrylic acid by boiling with fused sodium acetate in acetic anhydride was unsuccessful, for decomposition took place, the liquor rapidly darkening and soon becoming black.

The *phenylhydrazone*, $C_3H_3N_2 \cdot CH{:}N \cdot NHPh$, separated with the evolution of heat as a white, crystalline powder when 0·5 gram of the base and 0·6 c.c. of phenylhydrazine were ground together. After the mixture had been gently warmed on the water-bath to complete the reaction it was diluted with ether and filtered, when 0·85 gram of the hydrazone was obtained, melting at 187—190°. After crystallisation from alcohol, it formed prisms melting at 199—200° (corr.). It is sparingly soluble in water, alcohol, or acetone:

Found, C = 64·0; H = 5·4; N = 30·3.

$C_{10}H_{10}N_4$ (186·1) requires C = 64·5; H = 5·4; N = 30·3 per cent.

2-Phenyl-4-[1-acetylglyoxaline-4(or 5)-methylidene]-oxazolone, $C_{15}H_{11}O_3N_3$.

2·5 Grams of glyoxalineformaldehyde, 4·5 grams of hippuric acid, and 2·5 grams of fused sodium acetate were ground together, mixed with 10 c.c. of acetic anhydride, and heated on the water-bath. The solids quickly dissolved, giving a clear, dark brown, fused mass, which soon began to deposit well-formed, prismatic, yellow needles. After heating for half an hour the mass was cooled, filtered off, and washed with alcohol. The crystals were then ground with cold water, washed with water and alcohol, and dried in the air. The yield amounted to from 5·0 to 5·6 grams, that is, 68 to 76 per cent. of the theoretical, and the product was pure,

* By the oxidation of histidine, Fränkel (*Beitr. chem. Physiol. Path.*, 1907, **10**, 116) obtained a neutral by-product melting at 300° together with glyoxaline-4(or 5)-glyoxylic acid. He suggested that this was probably glyoxalineformaldehyde, but it is now clear that it could not have been so, since the pure substance melts at 173—174° (corr.).

the melting point remaining unchanged after recrystallisation of the substance.

The *oxazolone* crystallises from chloroform in bright yellow needles melting at 191° (corr.). It is insoluble in water, very sparingly soluble in cold alcohol, ether, acetone, or benzene, sparingly so in cold chloroform, but readily so in hot chloroform:

Found, C = 64·0, 63·5; H = 3·9, 3·9; N = 15·2, 15·0.

$C_{15}H_{11}O_3N_3$ (281·1) requires C = 64·0; H = 3·9; N = 14·9 per cent.

It is gradually dissolved by boiling with hot alcohol, but appears to decompose under these conditions. It does not readily dissolve in cold dilute acids or alkalis. When covered with 10 per cent. aqueous hydrochloric acid, it is converted into a pale yellow powder, and on diluting the mixture and filtering, a clear, colourless filtrate results. When this is basified with aqueous sodium carbonate, a bright yellow colour is developed at first, and then an amorphous, yellow precipitate is deposited. The oxazolone is decomposed by heating with dilute mineral acids, forming benzoic and acetic acids, and presumably also glyoxalinepyruvic acid and ammonia. It yields α-benzoylamino-β-glyoxaline-4(or 5)-acrylic acid in good yield when boiled with dilute aqueous sodium carbonate, and is decomposed with evolution of ammonia when boiled with aqueous sodium hydroxide.

α-Benzoylamino-β-glyoxaline-4(or 5)-*acrylic Acid*, $C_{13}H_{11}O_3N_3$.

Five grams of the oxazolone were boiled with a solution of 2·5 grams of anhydrous sodium carbonate in 125 c.c. of water until completely dissolved (about fifteen minutes). The solution was treated with animal charcoal, filtered, and mixed with 1·76 grams of glacial acetic acid. The liquor set to a mass of colourless crystals, which were collected, washed, and dried in the air. The yield was 4·3 grams of the hydrated acid, that is, 88 per cent. of the theoretical.

α-Benzoylamino-β-glyoxaline-4(or 5)-*acrylic acid* crystallises from water in fine, colourless, glistening needles, which, after drying at 100°, melt and decompose at 208° (corr.). It is sparingly soluble in hot water and very sparingly so in cold water or alcohol. It is readily soluble in cold dilute mineral acids or alkalis, but not in dilute acetic acid:

Found, air-dried substance lost 6·7 per cent. at 100°.

$C_{13}H_{11}O_3N_3,H_2O$ requires H_2O = 6·5 per cent.

Found, in substance dried at 100°, C = 60·4; H = 4·5; N = 16·4.

$C_{13}H_{11}O_3N_3$ (257·1) requires C = 60·7; H = 4·2; N = 16·3 per cent.

Aqueous solutions of this acid immediately reduce cold aqueous

potassium permanganate, and solutions in aqueous sodium carbonate give a deep red coloration with aqueous sodium diazobenzene-*p*-sulphonate.

The *hydrochloride* crystallises from water in bundles of prismatic needles. It is anhydrous and melts at 229° (corr.), turning brown and then black. It is readily soluble in cold, very easily so in hot water:

Found, C = 53·0; H = 4·2; Cl = 11·9.

$C_{13}H_{11}O_3N_3,HCl$ (293·6) requires C = 53·1; H = 4·1; Cl = 12·1 per cent.

The *picrate* crystallises from water in rosettes of yellow prisms, which after drying at 100° melt and decompose at 212° (corr.). It is fairly readily soluble in hot water, sparingly so in cold.

*Benzoyl-*r*-histidine*, $C_{13}H_{13}O_3N_3$.

9·7 Grams of α-benzoylamino-β-glyoxaline-4(or 5)-acrylic acid suspended in 97 c.c. of water were shaken with 97 grams of 2 per cent. sodium amalgam, which was added gradually during three-quarters of an hour without cooling the solution. The clear, pale brown liquor was decanted from the mercury, mixed with 21 c.c. of 33 per cent. aqueous sodium hydroxide, and boiled until ammonia was no longer evolved, and subsequently for ten minutes. The solution was digested with animal charcoal, filtered, and neutralised to litmus with hydrochloric acid, when 3·65 grams of benzoyl-*r*-histidine (m. p. 244°) crystallised out. The mother liquor on concentration gave a second crop of 1·3 grams (m. p. 232°). The crude product was recrystallised from water, and gave 4·1 grams of pure benzoyl-*r*-histidine, that is, 42 per cent. of the theoretical yield.

*Benzoyl-*r*-histidine* crystallises from water in hard, glistening prisms containing one molecular proportion of water of crystallisation, which is lost at 115°, but not at 100°. It melts and decomposes at 248° (corr.) after turning yellow from about 235°. It is somewhat sparingly soluble in hot water, very sparingly so in cold water or alcohol. It is readily soluble in cold dilute mineral acids or alkalis, but not in dilute acetic acid:

Found, in air-dried substance, loss at 100° = nil; loss at 115° = 6·8.

$C_{13}H_{13}O_3N_3,H_2O$ requires H_2O = 6·5 per cent.

Found, in substance dried at 115°, C = 60·2; H = 5·1; N = 16·2.

$C_{13}H_{13}O_3N_3$ (259·1) requires C = 60·2; H = 5·1; N = 16·2 per cent.

Aqueous solutions of this acid do not readily reduce cold aqueous potassium permanganate. A solution of the acid in aqueous

sodium carbonate gives a deep red coloration with sodium diazobenzene-*p*-sulphonate.

The *hydrochloride* crystallises from water in hard, glistening prisms, which melt and effervesce at 232° (corr.). It is anhydrous, and is readily soluble in cold, very easily so in hot water:

Found, C=52·7; H=4·9; Cl=11·9.

$C_{13}H_{13}O_3N_3,HCl$ (295·6) requires C=52·8; H=4·8; Cl=12·0 per cent.

The *picrate* crystallises from water in bunches of glistening, feathery, yellow needles which, after drying at 100°, melt and decompose at 226° (corr.). It is fairly readily soluble in hot water, sparingly so in cold.

*Hydrolysis of Benzoyl-*r*-histidine. Formation of* r*-Histidine.*

Two grams of benzoyl-*r*-histidine and 120 c.c. of 20 per cent. aqueous hydrochloric acid were boiled for four hours under a reflux condenser. The solution was cooled and extracted with ether to remove the benzoic acid formed, and then evaporated to dryness in a partial vacuum. The residue, dissolved in a little water and mixed with a solution of hydrogen chloride in alcohol, deposited crude, crystalline *r*-histidine dihydrochloride melting at 210°. In order to purify this substance it was dissolved in water, and the solution was neutralised with aqueous sodium carbonate, digested with animal charcoal, filtered, and mixed with a hot concentrated aqueous solution of 3·3 grams of picric acid. On cooling, 3·1 grams of *r*-histidine dipicrate separated, and a further quantity of 0·4 gram was obtained from the mother liquors. The total yield, 3·5 grams, of this substance represents 70 per cent. of that theoretically possible. *r*-Histidine dipicrate sintered from 100° and melted at 103° (corr.) after drying in the air. A specimen of the same substance previously synthesised by the action of ammonia on *α*-chloro-*β*-glyoxaline-4(or 5)-propionic acid, and a mixture of the two, behaved similarly. After drying at temperatures below 100° both substances melted indefinitely between 140° and 150°, and the conditions of drying necessary for the salt to melt at 190° (corr.) were not rediscovered (compare T., 1911, **99**, 1397). On analysis the salt was found to have the composition previously recorded. (Found, C=33·2; H=3·0; H_2O=5·6. $C_6H_9O_2N_3,2C_6H_3O_7N_3,2H_2O$ requires C=33·3; H=3·0; H_2O=5·5 per cent.)

For complete identification of the substance, the picrate was converted into the dihydrochloride, and this into the base in the usual manner. The properties of both compounds agreed with

those previously recorded for *r*-histidine prepared by the action of ammonia on α-chloro-β-glyoxaline-4(or 5)-propionic acid. Thus, analysis of the dihydrochloride gave the figures C=31·6; H=4·9; Cl=30·9; $C_6H_9O_2N_3,2HCl$ requiring C=31·6; H=4·9; Cl=31·1 per cent. This salt melted and decomposed at 235° (corr.), whilst a specimen prepared by the previous method and a mixture of the two specimens melted and decomposed at 237° (corr.) in the same bath. The free base crystallised from water in quadrilateral plates which decomposed at 284° (corr.).

Glyoxaline-4(or 5)-*formaldehydecyanohydrin*, $C_3H_3N_2{\cdot}CH(OH){\cdot}CN$.

One gram of glyoxalineformaldehyde was dissolved in 2·5 c.c. of a saturated aqueous solution of sodium hydrogen sulphite. The solution became warm, and on the addition of a solution of 1·0 gram of potassium cyanide in 1·3 c.c. of water more heat was developed. On stirring and cooling, the solution quickly deposited the cyanohydrin in colourless, sandy crystals, which were collected, washed with a few drops of water, and drained on porous porcelain. The crude product amounted to 1·05 grams, and melted at 105°. It was quickly recrystallised from water, and a small portion separated in rosettes of prismatic needles which melted and decomposed at 115° (corr.):

Found, in air-dried substance, C=49·1; H=4·3.

$C_5H_5ON_3$ (123·1) requires C=48·8; H=4·1 per cent.

This substance is readily soluble in warm water, but sparingly so in ether or chloroform. It is easily decomposed when heated either alone or with solvents, yielding glyoxalineformaldehyde.

β-Hydroxy-β-glyoxaline-4(or 5)-*ethylamine*, $C_3H_3N_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2$.

Three grams of glyoxalineformaldehyde were converted into the cyanohydrin by the method given above, and the crude product was reduced by the process employed by Meister, Lucius, & Brüning (D.R.-P. 193634) for the reduction of protocatechualdehydecyanohydrin to β-3:4-trihydroxyphenylethylamine. The cyanohydrin was dissolved in 40 c.c. of 2·5 per cent. aqueous hydrochloric acid and stirred at −5° to −3°, whilst 90 grams of 4 per cent. sodium amalgam were added gradually and sufficient (about 120 c.c.) 5 per cent. aqueous hydrochloric acid was added simultaneously to keep the solution as nearly neutral as possible. The operation was complete in one hour. The aqueous solution was then filtered and mixed with 1 litre of cold saturated aqueous picric acid. 6·1 Grams of the required picrate separated almost

immediately in a pure state, the melting point being unchanged after recrystallisation of the salt from water. This yield is 32 per cent. of the theoretical calculated on the glyoxalineformaldehyde.

β-Hydroxy-β-glyoxaline-4(or 5)-*ethylamine dipicrate* crystallises from water in orange-yellow hexagonal plates or in serrated spikes. It is fairly readily soluble in hot, sparingly so in cold water. It contains $1H_2O$, which is not lost at 120°, and on heating sinters slightly from about 165° and melts and decomposes at 225° (corr.):

Found, in salt dried at 100°, C = 34·1, 33·9, 33·8; H = 2·9, 3·0, 2·8.

$C_5H_9ON_3,2C_6H_3O_7N_3,H_2O$ (603·2) requires C = 33·8; H = 2·8 per cent.

The *dihydrochloride* was prepared by decomposing the picrate with hydrochloric acid, removing the picric acid with ether, evaporating the acid solution to low bulk, and adding absolute alcohol. The salt crystallised in colourless needles, which melted and decomposed at 216° (corr.). It is anhydrous and is readily soluble in water, giving an acid solution, but insoluble in absolute alcohol:

Found, C = 30·5, 30·6; H = 5·5, 5·6; N = 21·5; Cl = 35·3.

$C_5H_9ON_3,2HCl$ (200·0) requires C = 30·0; H = 5·5; N = 21·0; Cl = 35·5 per cent.

This salt gives a deep red colour with sodium diazobenzene-*p*-sulphonate in alkaline solution. It gives no precipitate in aqueous solution with platinic chloride, gold chloride, mercuric chloride, or Meyer's reagent.

The *platinichloride* was prepared by mixing equivalent quantities of concentrated aqueous solutions of the dihydrochloride and platinic chloride and adding alcohol, when it separated in microscopic orange prisms containing $3H_2O$. (Found, H_2O = 8·8. Calc., H_2O = 9·1 per cent.) It begins to darken at 225° and gradually blackens up to 244° (corr.), when decomposition of the solid mass occurs. It is readily soluble in cold water, but very sparingly so in alcohol:

Found, Pt = 36·3.

$C_5H_9ON_3,H_2PtCl_6$ requires Pt = 36·3 per cent.

Glyoxaline-4(or 5)-*carboxylic Acid*, $C_3H_3N_2{\cdot}CO_2H$.

This substance crystallises from water in bunches of slender needles, which attain some length when crystallisation is slow. When placed in a bath at 100° and heated slowly, it melts and effervesces at 275° (corr.); when placed in a bath at 270°, at 284° (corr.). The melted product resolidifies on cooling, and then melts

at 88°, the melting point of glyoxaline. Knoop (*loc. cit.*), who previously observed the formation of glyoxaline in this way, gives the melting point of the acid as 286°. His statement that the acid is readily soluble in water requires correction, for it is only sparingly soluble in cold water, although readily so in hot. Thus 1·0 gram of the acid required about 20 c.c. of boiling water for complete solution, and, on cooling, 0·86 gram crystallised from the solution. The acid is therefore soluble to the extent of less than 1 per cent. in cold water.

The acid is anhydrous. (Found, C = 42·8; H = 3·7. Calc., C = 42·9; H = 3·6 per cent.) It forms salts both with acids and bases. The *sodium* salt crystallises well.

The *hydrochloride* crystallises from water in clusters of microscopic prisms, which are anhydrous. It effervesces at 262° (corr.) and the molten residue crystallises on cooling. This salt is readily soluble in cold, very readily so in hot water:

Found, C = 32·5; H = 3·4; Cl = 23·9.

$C_4H_4O_2N_2,HCl$ (148·5) requires C = 32·3; H = 3·4; Cl = 23·9 per cent.

The *nitrate* crystallises from water in prisms, which are anhydrous. It effervesces at 200°, then resolidifies, and melts again at about 270°. It is readily soluble in cold, very readily so in hot water:

Found, C = 27·7; H = 3·0.

$C_4H_4O_2N_2,HNO_3$ (175·1) requires C = 27·4; H = 2·9 per cent.

The *picrate* crystallises from hot water in small plates containing $1\frac{1}{2}H_2O$ (Found, H_2O = 7·5. Calc., H_2O = 7·3 per cent.), which are lost at 100°. After drying at 100°, it begins to melt at 195°, and forms a clear liquid at 215° (corr.), then effervesces. It is readily soluble in hot, sparingly so in cold water:

Found in salt dried at 100°, C = 35·2; H = 2·2.

$C_4H_4O_2N_2,C_6H_3O_7N_3$ (341·1) requires C = 35·2; H = 2·1 per cent.

Glyoxalinecarboxylic acid dissolved in aqueous sodium carbonate couples with sodium diazobenzene-*p*-sulphonate, giving a carmine dye, but its methyl and ethyl esters fail to do so.

All attempts to form the acid chloride of glyoxalinecarboxylic acid by the action of thionyl chloride or phosphorus pentachloride, either alone or in the presence of phosphoryl chloride, acetyl chloride, etc., on the acid, its ethyl ester or their salts, were quite unsuccessful, the substances remaining unaltered.

Ethyl Glyoxaline-4(or 5)-*carboxylate*, $C_3H_3N_2 \cdot CO_2Et$.

Five grams of glyoxalinecarboxylic acid hydrochloride were boiled with 25 c.c. of absolute alcohol for six hours under a reflux condenser, the liquor being saturated from time to time with dry hydrogen chloride. The salt gradually passed into solution, and at the end of this time the alcohol was removed by distillation. The residue was dissolved in a small quantity of water and precipitated with a saturated solution of potassium carbonate, when, on stirring, 3·6 grams of the ester were obtained as a sandy precipitate melting at 158°.

Ethyl glyoxaline-4(or 5)-*carboxylate* crystallises from alcohol in clusters of plates which melt at 162° (corr.). It is sparingly soluble in cold, more readily so in hot water, fairly readily soluble in cold alcohol and readily so in ether or chloroform. It is anhydrous:

Found, C = 51·2; H = 5·7.

$C_6H_8O_2N_2$ (140·1) requires C = 51·4; H = 5·7 per cent.

On hydrolysis by boiling with 10 per cent. aqueous hydrochloric acid, the acid is formed in quantitative yield.

Methyl Glyoxaline-4(or 5)-*carboxylate*, $C_3H_3N_2 \cdot CO_2Me$.

This ester was prepared in a similar manner. It crystallises from methyl alcohol in clusters of plates which melt at 156° (corr.). Its solubilities are similar to those of the ethyl ester, except that it is more sparingly soluble in cold methyl and ethyl alcohols:

Found, C = 47·6; H = 4·8.

$C_5H_6O_2N_2$ (126·1) requires C = 47·6; H = 4·8 per cent.

4(or 5)-[*Glyoxaline*-4(or 5)-*methyl*]-*glyoxaline*-5(or 4)-*methyl Alcohol*, $C_3H_3N_2 \cdot CH_2 \cdot C_3H_2N_2 \cdot CH_2 \cdot OH$.

This base was obtained as a by-product in the preparation of 4-(or 5)-hydroxymethylglyoxaline by the action of nitric acid on 2-thiol-4(or 5)-aminomethylglyoxaline (T., 1911, **99**, 673). After the crystallisation of a large quantity of hydroxymethylglyoxaline as hydrogen oxalate in well-formed crystals, the mother liquors deposited a powdery salt which melted at 80—120°. Forty grams of this salt were mixed with an excess of aqueous barium hydroxide, filtered, saturated with carbon dioxide, and again filtered. The liquor was acidified with hydrochloric acid, evaporated to a syrup, and stirred with absolute alcohol, when 7·2 grams of the hydrochloride of glyoxalinemethylglyoxalinemethyl alcohol were obtained

in a pure, crystalline condition, whilst another 4·5 grams, equally pure, were isolated from the mother liquor.

The base was obtained by dissolving 5 grams of the hydrochloride in water, adding 4 grams of anhydrous potassium carbonate, evaporating to dryness, and extracting with absolute alcohol. The residue left on distilling the alcoholic extract crystallised on the addition of a little water, 4·3 grams of the air-dried base being obtained.

Glyoxalinemethylglyoxalinemethyl alcohol crystallises from water in colourless, silky needles which contain $2H_2O$. (Found, $H_2O=16·4$, 16·7. Calc., $H_2O=16·8$ per cent.) It loses $2H_2O$ at 100°, and then melts at 174° (corr.). It is readily soluble in hot, but sparingly so in cold water:

Found, C = 54·3, 53·7; H = 5·5, 5·6; N = 31·5.

$C_8H_{10}ON_4$ (178·1) requires C = 53·9; H = 5·7; N = 31·5 per cent.

The *hydrochloride* crystallises from water or dilute alcohol in prisms, which are anhydrous and melt at 178—179° (corr.). It is very readily soluble in water and very sparingly so in cold alcohol:

Found, C = 38·7, 38·5; H = 4·7, 4·8; Cl = 28·3, 28·1.

$C_8H_{10}ON_4,2HCl$ (251·1) requires C = 38·2; H = 4·9; Cl = 28·3 per cent.

The *hydrogen oxalate* crystallises from water with $1H_2O$. (Found, $H_2O=5·4$, 5·2. Calc., $H_2O=4·8$ per cent.) After drying, it melts and effervesces at 165° (corr.). It is sparingly soluble in cold, but readily so in hot water:

Found, in anhydrous salt, C = 40·3; H = 3·9.

$C_8H_{10}ON_4,2C_2H_2O_4$ (358·2) requires C = 40·2; H = 3·9 per cent.

The *picrate* separates in long, broad needles from hot water. It is anhydrous and melts at 197—198° (corr.). It is fairly readily soluble in boiling water, very sparingly so in cold water:

Found, C = 38·1, 37·7; H = 2·5, 2·7.

$C_8H_{10}ON_4,2C_6H_3O_7N_3$ (636·2) requires C = 37·7; H = 2·5 per cent.

Glyoxalinemethylglyoxalinemethyl alcohol was recovered unchanged after heating (1) for three hours at 170° with ten times its weight of concentrated hydrochloric acid, and (2) for three hours at 190° with twenty times its weight of 50 per cent. sulphuric acid.

Both the alcohol and its benzoate yield a carmine solution when mixed with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

Glyoxalinemethylglyoxalinemethyl benzoate was prepared by the action of benzoyl chloride on the alcohol. The method of preparation was precisely similar to that of glyoxalinemethyl benzoate

(T., 1912, **101**, 541), except that the acid solution was precipitated by the addition of sodium carbonate, when the benzoate separated as an oil which soon crystallised. The crystals melted at 67—68° (corr.), and the same melting point was recorded after the substance had been crystallised from water, when it separated in needles containing water of crystallisation:

Found, $H_2O = 8{\cdot}7$.

$C_{15}H_{14}O_2N_4, 1\frac{1}{2}H_2O$ requires $H_2O = 8{\cdot}7$ per cent.

After crystallisation from ethyl acetate, the substance is obtained anhydrous in the form of warts melting at 120—121° (corr.):

Found, $C = 63{\cdot}9$; $H = 5{\cdot}0$; $N = 20{\cdot}0$.

$C_{15}H_{14}O_2N_4$ (282·1) requires $C = 63{\cdot}8$; $H = 5{\cdot}0$; $N = 19{\cdot}9$ per cent.

The substance is sparingly soluble in cold, but fairly readily so in hot water; readily soluble in alcohol or chloroform, but sparingly so in ether. It dissolves readily in dilute hydrochloric acid.

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XXIII.—*The Preparation and Properties of Colloidal Carbon.*

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THE existence of carbon in colloidal solution has been the subject of a number of investigations. Between 1879 and 1885 Bartoli and Papasogli in a series of papers (*Atti R. Accad. Lincei*, 1879—1880, **8**, 89; *Nuovo Cim.*, 1880, [iii], **8**, 278; 1881, **10**, 207; 1883, **12**, 141; *Naturforsch.*, **14**, 122; *J. Physique*, **10**, 458; *Gazzetta*, 1881, **11**, 237, 468; 1882, **12**, 113, 117, 125; 1885, **15**, 461) described the production of an organic compound by the electrolysis of various solutions with carbon electrodes. The subject was further investigated by Coehn (*Zeitsch. Elektrochem.*, 1896, **2**, 544, 616; 1897, **3**, 424) and Vogel (*Zeitsch. Elektrochem.*, 1897, **3**, 581, 680; 1898, **4**, 123) more from a chemical than from a colloidal point of view. Bredig does not mention carbon among the hydrosols he produced by the electric discharge method (*Zeitsch. angew. chem.*, 1898, **11**, 951); and similarly Svedberg describes no carbon hydrosol in his early paper (*Ber.*, 1905, **38**, 3616), but later (*Ber.*, 1906, **39**, 1705) mentions a carbon sol in *iso*butyl alcohol and other organic solvents in which, indeed, carbon appears to be formed in the colloidal condition on the decomposition of the

medium itself when sparks are passed under the surface. Degen [*Diss.* (Greifswald, 1903)] obtained a sol in ethyl alcohol by electric dispersion, but not in water; Thomae (*Kolloid Zeitsch.*, 1912, **11**, 268) obtained a stable sol in dilute aqueous sodium hydroxide, but not in pure water; similarly, Vanzetti (*Kolloid Zeitsch.*, 1913, **13**, 6) with purified carbon electrodes formed a negative sol the solid matter from which gave carbon monoxide and carbon dioxide as well as water when heated in a vacuum. Sabbatani (*Kolloid Zeitsch.*, 1914, **14**, 29) formed a carbon sol by dehydrating sugar with sulphuric acid and pouring the product into water. Concurrently, Acheson (*Trans. Amer. Electrochem. Soc.*, 1907, **12**, 29; *J. Soc. Chem. Ind.*, 1907, **26**, 157) had developed on a commercial scale the production of carbon which, in some cases, appeared to be colloidal, for lubrication and other purposes This paper is an attempt to amplify some of these researches and to correlate the results as far as is possible.

Experimental.

Finely powdered sucrose was gradually added as in Sabbatani's preparation to concentrated sulphuric acid, the proportions being 1 gram of sucrose to 10 c.c. of acid. The most effective method of adding the sucrose was to place it in a funnel with a narrow neck, the funnel being inserted in the neck of a flask containing the acid; the flask was gently shaken by hand with a rotatory movement, thus causing the sucrose to drop little by little into the acid. More vigorous shaking (for example, in a machine) resulted in the formation of lumps in the liquid. When all the sucrose was added, the liquid was allowed to remain for twenty-four hours, and was then poured into four times its volume of cold distilled water. The whole was then filtered to remove the larger particles which were always present to a greater or less degree.

The filtrates obtained in this way varied in colour from yellow to dark reddish-brown, which seemed to depend largely on the accidental formation of lumps in the process of preparation. On dialysis through parchment paper, much of the acid diffused out first, but afterwards the outer liquid became yellow owing to the diffusion of other substances. In order to remove the last traces of sulphuric acid very prolonged dialysis was necessary. On examination in an electric field, the particles moved towards the anode, that is, were negatively charged. In the ultramicroscope not many particles were visible; and gold chloride was reduced by the dialysed filtrate, in some cases in the cold, but sometimes only on heating. On the addition of small quantities of electrolytes

(for example, when 0·5 c.c. of $N/20$-barium nitrate was added to 10 c.c. of the liquid) a cloudiness appeared, which finally settled to the bottom of the vessel as a brown powder. Even if a considerable quantity of electrolyte was added, no further precipitation occurred, and the substance, which coloured the solution brown, remained, presumably in ordinary solution, as it diffused (although slowly) through parchment paper.

The residue on the filter paper, after being washed with water, was soaked in sodium hydroxide solution, when some of it formed a liquid similar in properties to that described above. On dialysis, what did not pass through the paper was deposited as a precipitate.

Similar results were also obtained by the use of icing sugar instead of ordinary sucrose; dextrose and rice starch were also tried, but in these cases much more carbon was precipitated on dilution than with sucrose. When, before adding it to the acid, the sucrose was dissolved in a small quantity of water, the carbon and the soluble substance were found on the filter paper and in the filtrate respectively, no carbon being dispersed.

Experiments were made with dehydrating agents other than sulphuric acid. Fuming sulphuric acid and a hot solution of zinc chloride gave results similar to those obtained with sulphuric acid, except that the carbon produced was more compact and less suspended. With phosphoric oxide no action occurred if the mixture of it with the sugar was kept dry, but on addition of a drop either of sulphuric acid or of water a vigorous action took place with the formation of a spongy mass. On adding water and filtering, a liquid was obtained with similar properties to those obtained by the action of sulphuric acid.

Thus it is clear that although some carbon in the suspensoid state is produced by the dehydration of sucrose, etc., with excess of concentrated sulphuric acid, its properties are obscured by more complex products of decomposition, the presence of which is obvious from the odour of burnt sugar arising from the solution during the dehydration process or when evaporated to dryness on the water-bath. They do not appear to exert a protective action on the carbon.

When an electric current (0·4—4·0 amperes at 200 volts) is passed through dilute sodium hydroxide solution using carbon electrodes, one of the electrodes being immersed in the solution and the other just touching the surface, the liquid becomes dark owing to the disintegration of the electrodes. On filtration, most of the particles pass through the filter and, if the sol is then

diluted, remain suspended for many months; otherwise a slow deposition of some of the dispersed matter ensues, presumably removing excess of alkali.

On varying the positions and signs of the electrodes, it was found that most dispersion occurred when the positive pole just touched the surface of the liquid, thus giving a high current density at its surface; on immersing it further, electrolysis was more vigorous, but little dispersion occurred. With the negative pole touching the surface, an arc was set up between carbon and liquid and the electrode was burnt away, some large particles being formed from its violent disintegration. Only large particles could be obtained by striking an arc between the carbons under the surface. It was also found that almost all the sol originated from the positive pole, for when the other electrode was surrounded by a soaked thimble of parchment paper only the outer liquid became dark. Under ordinary conditions, however, if the current was reversed after it had been flowing for some time, a cloud of dark particles arose from the negative pole immersed in the liquid; this appears to be due to the removal from that pole of particles which were formed from the positive pole and were carried through the liquid and deposited by cataphoretic action.

Most of the sols were obtained from electrodes of ordinary arc carbons, but similar results were obtained with electrodes of crude gas carbon and of Acheson graphite.

A solution of sodium hydroxide containing 2—3 grams per litre is best for the formation of the sol; a more dilute solution does not permit a sufficiently heavy current to pass, whilst a greater concentration precipitates the sol, and the positive electrode is not so finely broken up. The formation of a sol is noticeable, however, at as low a concentration as 0·4 gram per litre, that is, $N/100$; and although a more concentrated solution is more efficient for the actual preparation, the sol is more stable if diluted soon after formation.

The sols thus obtained when subjected to dialysis in a bag or thimble of parchment paper are completely precipitated if the alkali is entirely removed in this manner; the dialysis can be stopped when just enough alkali is left to render the sol stable. (In this the sol is similar in behaviour to a ferric hydroxide sol, which is precipitated if all the acid is dialysed away from it.) The deposit formed in the dialyser can be suspended in part by addition of water containing a little alkali.

The sol showed a very distinct Tyndall cone, and in layers more than a few mm. in thickness was black; in very thin layers it was of a brown tint. Under the microscope no particles were seen,

but with the ultramicroscope a large number were visible in vigorous Brownian movement. Thus the particles were of a size similar to that of the particles in metallic sols.

When exposed to the action of an electric field in the ordinary Y-tube apparatus, the particles in the sols prepared invariably moved towards the anode, that is, they were negatively charged, as are most hydrosols of elements, whether metals or non-metals. If the sol was acidified, no change in the sign of the charge took place.

The sols were particularly sensitive to electrolytes, so much so that if tap-water was used in preparing them, precipitation of the particles occurred as fast as they were formed. An experiment with a sol containing about 0·3 gram of carbon per litre (by the loss in weight of the electrodes) and $N/40$-barium chloride gave the following results. Ten c.c. of the sol were used in all cases.

$N/40$-Barium chloride. c.c.	Result.
0·10, 0·15	No precipitate apparent at once; very slight precipitate after a week.
0·20, 0·25	No precipitate apparent at once; mostly precipitated after a week.
0·30, 0·40	Some aggregates after one hour; completely precipitated in a week.
0·50, 0·70	Some aggregates at once; partly settled in one hour.
0·80, 1·00	Flocculation at once; mostly settled in one hour.
3·00	Flocculation at once; mostly settled in twenty minutes.

Thus, taking 0·3 c.c. as the minimum concentration to effect precipitation of the sol employed, it will be seen that this concentration is one of 0·078 gram of barium chloride (that is, 0·36 millimol.) per litre of sol. This concentration is of the same order as that required to precipitate other suspensoids of similar dispersity and concentration (both of which in the case of sols used in this work were only approximately known). For example, an arsenic trisulphide sol containing 7·54 millimols. per litre required a concentration of 0·691 millimol. per litre of barium chloride to precipitate it (Freundlich, *Zeitsch. physikal. Chem.*, 1903, **44**, 144).

The coagulum from the sol was black, and was only partly dispersed again on prolonged washing with distilled water.

It was thus seen that the sols formed in this way were typical suspensoids; and it now remained to see whether the particles were pure carbon or a product of oxidation. With this end in view, the sol was made on a considerable scale, and after filtration and keeping was precipitated by barium chloride and the solid

collected in order to determine its composition by combustion. The precipitate was washed with distilled water and then with dilute hydrochloric acid to remove the barium carbonate which had gradually accumulated in the mass. On doing this, a yellow liquid passed through the filter; it was apparently not colloidal, as it gave no Tyndall cone and diffused easily through parchment paper. On distilling a portion of the filtrate, the coloured substance remained in the non-volatile portion, and on evaporation on the water-bath a small quantity of brown residue remained; if sulphuric acid was present during the evaporation, an odour of burnt sugar was noticeable, but there was not sufficient of the substance to permit of its identification.

The precipitate was washed with dilute hydrochloric acid until the filtrate gave no precipitate with dilute sulphuric acid; on finally washing with distilled water, some of the colloid passed through the filter paper, so it was washed with very dilute hydrochloric acid until the filtrate ceased to be yellow. It was then dried in the air for a week, ground, and kept for a similar period in a vacuum desiccator.

On burning it in oxygen in the ordinary apparatus for organic combustion, the following results were obtained:

	I.	II.	Mean values.
Carbon	65·73	67·50	66·61
Hydrogen	2·07	1·93	1·99
Residue	15·85	14·66	15·25
	83·65	84·09	83·85
Difference	16·35	15·91	16·15
	100·00	100·00	100·00

The "residue" remains unburnt even when heated to bright redness in pure oxygen, and on examination it was found to consist mostly of silica with a trace of iron. Thus it is probably derived from impurities in the arc carbons used to make the sol. The difference is presumably oxygen.

When the results are calculated on the basis of percentage of combustible material they agree fairly well with those obtained by Söhngen (*Chem. Weekblad*, 1914, **11**, 593), who obtained C = 81·2, H = 0·85, and O = 18 per cent., whilst the mean results in this work are C = 78·59, H = 2·35, O = 19·05 per cent.

It is clear that very considerable oxidation occurs during the disintegration of the electrodes, as organic compounds occur in the washings, and possibly in the above product. The results of analysis of the latter may point to the existence of a carbohydrate, or more likely to water firmly retained by the carbon; the latter seems probable in view of the washing of the precipitate until free

from coloured soluble matter, but in any case organic matter is present in the sol and seems necessary for a stable dispersion.

The carbon formed by the reduction of carbon dioxide with magnesium was prepared, and the crude product treated with dilute hydrochloric acid to remove magnesium oxide and carbonate. On powdering it and adding it to water, no permanent suspension was noted after some months, neither did the addition of alkali to the water cause a colloidal solution to be formed.

Silicon, when prepared in this way, readily forms a suspension (Astfalk and Gutbier, *Kolloid Zeitsch.*, 1914, **15**, 23).

When acetylene reacts with chlorine, a fine soot is produced. It was found to be impossible to produce it in water by simultaneously bubbling the two gases through the liquid. If produced by spontaneous combustion of the gases, it was difficult to moisten it and no suspension ensued.

Carbon, prepared by the dehydration of sucrose by sulphuric acid, was treated with excess of the acid in order to dehydrate, if possible, the intermediate compounds formed. The mass was then washed with water until free from acid, but it did not form a suspension either in water or alkali; a brownish-yellow solution was observed after some time in the alkali used, whilst in the aqueous liquid a fungus began to grow, showing that organic compounds were still present. Similarly, if the carbon was heated to a red heat either in air or in chlorine, the residue gave no sol with water or alkali.

The porous carbon which is the foundation of the forms of graphite sold by the Acheson Company is produced by heating in an electric furnace with insufficient calcium the mixture required to make calcium carbide (*J. Soc. Chem. Ind.*, 1907, **26**, 157). The porous carbon is ground, and can be suspended temporarily in oil or water, but if tannic acid or other organic substances are added to the water a permanent sol is formed (*Trans. Amer. Electrochem. Soc.*, 1907, **12**, 29). In making electrodes and crucibles, the sol is precipitated by electrolytes (for example, alum), moulded, and dried. It was found that a loss of carbon occurred in the process amounting to as much as 6 per cent. of the precipitate. This was accounted for by the formation of a yellow liquid in the water used in the "mastication" of the precipitate. This is probably the same as the yellow liquid washed out of the precipitates obtained by the second method above.

On examination of pieces of an Acheson graphite electrode, it was found that although they were more difficult to disintegrate when used in place of arc carbons in the electrolytic method, a similar sol was obtained. A finely powdered portion could not be

dispersed in water or alkali, but floated on the surface. However, on the addition of a few crystals of tannic acid to either solution, the powder was immediately dispersed to give a violet sol which had almost the same properties as those obtained by the electrolytic method. The precise action of the tannic acid has not yet been determined, but it may have a surface-tension effect, thus permitting the particles to be made wet, or it may exert a protective influence on the carbon particles.

Animal charcoal was extracted with concentrated hydrochloric acid to remove inorganic salts, and then well washed with water and dried. The powder thus obtained did not form a suspension in water, alkali, or tannic acid. When some of it was treated with about twenty times its weight of concentrated sulphuric acid, a brown liquid was obtained. On dilution with water to ten times the volume, almost the whole was precipitated in brownish-black flocks, which when filtered and washed were suspended, but only for a short time, both in alkali and in tannic acid. Pattison (*J. Soc. Chem. Ind.*, 1903, **22**, 608) has obtained the sulphuric acid solution, and regards it as evidence that organic matter is still left in animal charcoal, and to this he attributes the superior adsorptive power of such charcoal over other varieties of carbon. Comparing these results with the others obtained in this work, they seem to confirm the supposition of the existence of organic matter in the charcoal.

Conclusions.

It appears that in order to produce a stable suspensoid sol of carbon particles in water, the following conditions are necessary:

(1) The carbon must be in a special state, so that it is easily disintegrated.

(2) Organic matter must either be added to, or formed in, the liquid.

(3) Alkali aids the suspension, although it is not essential in some cases, but it is probable that in all cases a trace of some electrolyte is necessary to ensure stability of the sol.

I have to thank Mr. E. Hatschek for bringing to my notice the subject of this investigation, and also Dr. C. A. Keane and Dr. R. S. Willows for kind interest and fertile suggestions during its course.

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XXIV.—*A Product Obtained in the Manufacture of Natural Indigo.*

By Arthur George Perkin.

Among the few points connected with the manufacture of natural indigo which do not appear to have received attention is the so-called 'seeth water,' the liquid from which the indigo precipitate settles out at the conclusion of the oxidation process. An examination of this product was suggested by Sir Lewis Hay, Bart., and also by Lieut.-Colonel Ranking, who kindly supplied samples of the evaporated material in the hope that further evidence might thus be forthcoming which would be of value to the industry.

Experimental.

Three samples of evaporated 'seeth water' were available for examination. The first and most important of these (*a*) was derived from water drawn from an oxidation vat in the Purtabphore factory in India, and represented 0·75 per cent. of the original liquid. In the process of manufacture, 100 parts of the plant (*Indigofera sumatrana*) underwent fermentation in the presence of 540 parts of water, so that very approximately the residue corresponded with 4 per cent. of the plant. On the other hand, the yield of cake indigo was 0·2328 per cent., but unfortunately the analytical value of this and of the plant itself could not be ascertained. Sample (*b*) consisted of evaporated drainings from the 'mahl table,' or filter, at the same factory, and formed 0·77 per cent. of the original liquid, whereas the origin of sample (*c*), supplied by Colonel Ranking, was doubtful.

These products consisted of resinous lumps varying in colour from yellowish-brown to deep brown. They were extremely hygroscopic, and when ground emitted an odour resembling that of decayed cheese.

When incinerated, the amount of ash given in each case was very similar, namely:

(*a*) 27·23, (*b*) 25·90, (*c*) 26·87 per cent.

This was not quantitatively examined, but consisted mainly of the oxides of calcium, magnesium, and potassium, traces of manganese oxide and alumina being also present.

The estimations of nitrogen in these samples were carried out by Khejdahl's method, the combustion of the substances described by means of copper oxide being very tedious. Pre-

liminary trials, employing pure indigotin, carried out some years ago by the late W. P. Bloxam and the author, indicated that if in this process 100 per cent. sulphuric acid (monohydrate) and potassium sulphate are employed, very accurate figures can be obtained. Experience, indeed, has shown that in these circumstances little or no difficulty occurs during the analysis of most organic nitrogenous materials.

Found: (*a*) N = 2·25; (*b*) N = 2·77; (*c*) N = 2·72 per cent.

Experiment indicated that ammonium salts were absent from these products.

The samples were neutral, in the main dissolved readily in water, and these liquids on acidification emitted a strong odour of volatile aliphatic acids. These were estimated by Grimshaw's method, which consists in treating the material with sodium hydrogen sulphate solution and ascertaining the acidity before and after removal of the volatile liquids by evaporation. The percentages are calculated as acetic acid, although much butyric acid was evidently present.

Found: (*a*) 23·8; (*b*) 21·04 per cent.

A search for anthranilic acid, isatin, and other well-defined products of the indole group in these mixtures gave only a negative result, and it soon became evident that the main constituents could not be isolated in a crystalline condition.

Seventy-five grams of (*a*) were agitated for about half an hour with 500 c.c. of boiling water, and, after cooling, the insoluble brown residue was removed. To eliminate mineral matter it was digested with boiling 1 per cent. hydrochloric acid, and the mixture when cold rendered alkaline and subsequently acidified. This procedure was necessary to facilitate filtration, which otherwise was difficult to carry out. The precipitate (*A*), when collected and dried at 100°, weighed 3·292 grams, whereas in a second similar operation 3·225 grams were isolated.

In appearance this product closely resembled indigo-brown, and it was therefore examined by the methods formerly employed (T., 1907, **91**, 279) in the investigation of this material.

By extraction with hot pyridine, 0·5485 gram remained undissolved, which when dry resembled a crude cake indigo, and yielded to boiling nitrobenzene 0·135 gram of crystalline indigotin, or 0·18 per cent. of the original material.

As is well known, owing to the incomplete settlement of the indigo precipitate, some quantity is drained away by the 'seeth water,' which according to Rawson ("Report on the Cultivation and Manufacture of Indigo," 1907, p. 86) "frequently contains as

much as 20 per cent. of the total colouring matter produced." In the present case, if the 0·2328 per cent. of cake indigo yielded by the plant be given the average value of 60 per cent. purity, then the loss of indigotin or of cake indigo indicated by the above result will be 5·2 per cent. The value of this figure naturally depends upon the accuracy of the method employed for the sampling of the 'seeth water,' which in respect of the suspended matter present would be a difficult operation.

The pyridine filtrate on treatment with excess of boiling alcohol yielded a deposit of the main bulk of the brown matter (*A*), and this was well washed and dried at 160°. To ascertain the effect of subsequent purification, it was submitted to analysis.

Found: C=63·59; H=5·07; N=7·39 per cent.

Extraction with boiling acetic acid removed a small amount of a soluble compound evidently possessing a low nitrogen content, and the residue was now dissolved in pyridine and precipitated with alcohol.

Found: C=65·70; H=5·07; N=8·03 per cent.

It consisted of a dark brown, amorphous powder, indistinguishable in general property from the main constituent of indigo-brown. The composition assigned to the latter is: C=68·57; H=4·28; N=10·0 per cent. (*loc. cit.*), whereas the very similar product derived from the decomposition of indoxylic acid (T., 1909, **95**, 848) gave: C=67·35; H=3·68; N=9·94 per cent. This 'seeth water' brown is thus more highly oxygenated. By digestion with boiling 50 per cent. potassium hydroxide solution, a trace of anthranilic acid was produced.

The filtrate from *A* on treatment with ether gave some quantity of brown precipitate, which was well washed and dried at 160°.

Found: C=64·70; H=5·00; N=4·57 per cent.

The brown matter in 'seeth water' thus consists of a mixture of compounds of variable nitrogen content.

A somewhat similar precipitate can be obtained from the aqueous extract of *Indigoferae* leaves, which in the case examined (*loc. cit.*) contained 5·67 per cent. of nitrogen, and this was presumably derived in part from the indican present.

It has been previously shown (T., 1908, **95**, 803) that by the action of hydrochloric acid, indican gives indoxyl-brown, and the yield is such that the main bulk of the original nitrogen is contained by this product. A further experiment showed that by nearly neutralising the acid filtrate obtained when isolating this substance, and evaporating to dryness, a further quantity of a brown material can be recovered by means of water, in which

almost all the nitrogen previously unaccounted for is present. The latter itself contained but 2·5 per cent. of nitrogen, so that evidently here a decomposition of the dextrose had also taken place.

2·442 Grams of indican gave 1·112 of indoxyl-brown (N = 9·42) and 0·3187 of brown matter (N = 2·5). The nitrogen present in these decomposition products was thus 97·4 per cent. of that contained by the indican.

From this result it suggested itself that by a comparison of the leaf brown and 'seeth water' brown, as regards nitrogen content, it would be possible to ascertain what amount of the latter was due to the alteration of indoxyl during the process of manufacture. Such an experiment, however, proves to be impracticable outside the actual factory, for numerous samples of the air-dried leaf kindly supplied for this purpose by Sir Lewis Hay had so deteriorated in transit that they contained little or no indican on arrival.

Moreover, again, Prof. E. R. Watson, of Dacca, was good enough to investigate the effect of air-drying on the indican of the leaf, with the result that a disappearance of some quantity of this compound was thus found to occur.

The neutral filtrate (*B*) from the crude brown matter was now treated with 300 c.c. of *N*-sulphuric acid, an amount found necessary by the titration of the ash residue alluded to above, the product evaporated until syrupy, and then stirred with boiling alcohol to precipitate mineral matter. Addition of ether to the supernatant liquid, which possessed a greenish-blue fluorescence, caused the separation of a brown, viscous mass, which was washed two or three times with ether. The product was treated with water, and a trace of brown matter removed from the solution, which on evaporation yielded 19 grams of residue. By re-solution in alcohol and precipitation with ether, an almost colourless material was ultimately isolated. When dry it consisted of a friable mass, and to the presence of this substance the very hygroscopic nature of the dried 'seeth' residue was evidently due. If strongly heated it yielded a vapour possessing the odour of burnt feathers in which ammonia was present, and in general property closely resembled the so-called indigo gluten of crude indigo. Allowing for a trace of mineral matter, which it obstinately retained, this preparation contained 8·22 per cent. of nitrogen. The amount of this product in the 'seeth water' residue, although probably more than 20 per cent., could not be accurately determined, as loss occurs during the precipitation process described above, but there can be no doubt that it is mainly responsible for the nitrogen contained therein.

The supernatant ethereal liquids from which the gluten had sepa-

rated were evaporated to dryness, the residue treated with water, the solution freed from a trace of brown matter, and concentrated.

Crystals (1·66 grams) separated, and were purified by recrystallisation from water. (Found: C=40·67; H=5·14. $C_4H_6O_4$ requires C=40·67; H=5·08 per cent.)

These melted at 185—186°, required 67·8 per cent. of sodium hydroxide for neutralisation, when strongly heated yielded an anhydride melting at 118—119°, and had all the properties of succinic acid.

The mother liquors by evaporation gave a small amount of syrupy residue, in which some gluten and a little succinic acid appeared to be present. No well-defined third compound could be isolated from it.

The small amounts of brown substance obtained during the fractionations described above, when added to the main bulk (*A*) increased its weight to 3·90 grams, or 5·2 per cent. of the 'seeth water' residue. By directly treating the latter with dilute hydrochloric acid, a somewhat larger quantity, equivalent to 5·58 per cent., was obtained, which on analysis gave N=7·3 per cent.

'Mahl Table' 'Seeth Water' Residue.

This material when examined by the methods previously described yielded much more brown matter than the sample (*a*). Thus, whereas fractionation gave 12·03 per cent., the yield by the direct neutralisation method was 12·54 per cent. An analysis of the latter preparation gave N=6·87 per cent., and that this was a mixture was indicated by the isolation from it of a more readily soluble fraction, in which but 4·57 per cent. of nitrogen was present.

In the ordinary process of manufacture of natural indigo, the indigo precipitate before filtration is boiled in the so-called 'mahl boiler,' and that a purification here occurs is evident, in that brown matter originally carried down with the dye is removed by solution in the hot 'seeth water.' That samples (*a*) and (*b*) correspond fairly closely with one another is certain from the analytical results and from the fact that they represent respectively operations occurring in the same factory on July 17th and July 23rd, 1913.

The indigotin present was approximately 0·10 per cent. (0·0732 gram from 75 grams of the residue), a loss more trivial than in the former instance, the volume of liquid here dealt with being comparatively small, whereas succinic acid (1·63 grams, or 2·18 per cent.) and an indigo gluten fraction of considerable amount were also isolated.

Sample (c).

This product, of which only 25 grams were available, yielded 11·18 per cent. of brown matter containing N = 7·77 per cent., the indigotin present being estimated 0·082 per cent. No record of its origin was available, but as a close resemblance exists between the analytical results found with both this and sample (*b*), it is reasonable to presume that it was obtained by the evaporation of 'mahl table' 'seeth water.'

The following table illustrates the main results above recorded:

	a. Per cent.	*b.* Per cent.	*c.* Per cent.
Nitrogen	2·25	2·77	2·72
Ash	27·23	25·90	26·87
Volatile acids...	23·80	21·04	—
Succinic acid ...	2·21	2·18	—
Brown matter..	5·58	12·03	11·18
Indigotin	0·18	0·10	0·082

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XXV.—*The Simultaneous Estimation of Carbon and Halogen by the Chromic Acid Method.*

By PHILIP WILFRED ROBERTSON.

THE first successfully to estimate carbon by the action of chromic acid and sulphuric acid on organic compounds was Messinger (*Ber.*, 1890, **23**, 2756); traces of incompletely oxidised carbon, suspected to be carbon monoxide, were converted into carbon dioxide by passing the products of the reaction over heated copper oxide. The apparatus, however, was unduly complicated, and the time required for each estimation was very long. That carbon monoxide is actually produced by the action of the chromic–sulphuric acid mixture was proved by Cross and Bevan (T., 1888, **53**, 889), who attempted to estimate the carbon gasometrically. Their method, although rapid, suffered from the disadvantage that the estimation could not be carried out above 100°, at which temperature oxygen is evolved, and that an arbitrary correction had to be introduced to allow for the solubility of the carbon dioxide in sulphuric acid.

As was to be expected, Messinger's method was used only to a limited extent—in cases where the combustion of the substance was

impossible or difficult. Thus Thiele and Marais (*Annalen*, 1893, **273**, 151) obtained by its means good results for certain explosive tetrazole derivatives, and Küster and Shalberg (*Annalen*, 1894, **278**, 214), simplifying considerably the apparatus, employed it with success in the case of *iso*durene compounds, which had persistently given low values on combustion. Then, also, Fritsch (*Annalen*, 1896, **292**, 83) showed that it was possible to estimate both carbon and nitrogen in certain compounds, as the nitrogen remains in the reaction mixture in the form of an ammonium salt, and may be found by subsequent distillation with alkali.

As the chromic acid method proved so successful for the estimation of bromine and chlorine (T., 1915, **107**, 902),* it was hoped that these elements might be estimated simultaneously with the carbon. Actually this has already been attempted by Thies (*Chem. Zeit.*, 1914, **38**, 115) by passing the gases evolved from the chromic acid mixture first over heated lime, which retains the halogen and part of the carbon dioxide, and then through weighed soda-lime tubes to absorb the remaining carbon dioxide. The lime, which must be free from carbonate, is then treated with acid to free the remaining carbon dioxide, and the halogen is estimated in the solution. Such a procedure seems unduly complicated and tedious. It seemed preferable to absorb the halogen and the carbon dioxide together, and subsequently to determine each separately. In the first place, experiments were made to ascertain with what accuracy it was possible to estimate carbon by the chromic acid method.

Estimation of Carbon.

The apparatus used for this purpose was as in the figure, except that the absorption tubes were replaced by a calcium chloride tube, to retain traces of moisture, and two soda-lime tubes. To the reaction vessel was attached a short silica tube containing platinised asbestos, and between this and the absorption apparatus was a small U-tube containing glass wool well moistened with sulphuric acid containing chromic acid, to retain the oxides of sulphur. The substance to be analysed was weighed from a small

* I regret that at the time of publication of this paper I had not noticed that a method, the same in principle, had been described by Baubigny and Chauvanne (*Compt. rend.*, 1903, **136**, 1197). This method, an account of which is to be found in Weyl's "Handbuch" (Vol. 2, p. 1366), has been critically examined by Emde (*Chem. Zeit.*, 1911, **35**, 450). The apparatus, being somewhat complicated, is difficult to manipulate, and moreover is not capable of being employed for volatile substances; further, the use of excess of sodium sulphite as an absorbent has certain disadvantages, and lengthens considerably the time of an estimation.

tube into the reaction vessel, and to it was added about 3 grams of chromic acid. The air in the apparatus was then displaced by a stream of oxygen (fee from carbon dioxide), and the two soda-lime tubes, previously weighed full of oxygen, were attached. About 30 c.c. of redistilled sulphuric acid were poured by means of a small funnel into the reaction vessel, which was cooled externally by a beaker of cold water if the reaction tended to proceed too vigorously, and a slow current of oxygen was passed through the apparatus. In seventy to ninety minutes the combustion was finished, and the soda-lime tubes were weighed with the usual precautions. To test the chromic acid and sulphuric acid, blank experiments were performed under exactly the same conditions. With the materials and quantities employed, 0·0006 gram of carbon dioxide was obtained as the mean of three different determinations; this was accordingly subtracted from the weight of carbon dioxide found in each instance. In Table I are the results obtained for the compounds examined, such substances as might be expected to be oxidised with difficulty. The percentage values are calculated to one place of decimals, which represents the order of accuracy of the smaller weighing.

TABLE I.

Substance.	Weight.	Weight of carbon dioxide.	Found per cent.	Calc. per cent.
Anthraquinone	0·1081	0·3214	81·0	80·8
"	0·1051	0·3118	80·8	—
"	0·0648	0·1916	80·7	—
Thymol	0·1113	0·3262	79·8	80·0
Azobenzene.....	0·1118	0·3232	78·9	79·2
Substance *A**	0·1072	0·2650	67·4	67·4
Substance *B**	0·1020	0·2202	58·9	59·1
Trinitrophenol	0·1559	0·1806	31·6	31·4

* Cyanopiperidones, a group of compounds which tended to give low results on combustion, kindly placed at my disposal by Mr. G. A. R. Kon.

It is seen that the numbers compare favourably with those obtained by the ordinary combustion methods; even in the case of trinitrophenol, which might tend to give high values owing to the formation of oxides of nitrogen, there was good agreement.

It was further necessary to ascertain with what accuracy the carbon dioxide could be estimated volumetrically. The apparatus used for this purpose was that depicted in the figure. Each of the absorption tubes contained 10 c.c. of approximately 1·3 *N*-sodium hydroxide. The experimental details were as described under the estimation of carbon and bromine. Satisfactory results were obtained for various compounds with sodium hydroxide of this

strength, indicating that this simple absorption apparatus was sufficient completely to absorb the carbon dioxide.

A more accurate volumetric method for estimating carbon dioxide is with baryta, and as very dilute acid may be employed in the titration, a means was thus available for estimating the carbon in small quantities of organic compounds. For this purpose, the absorption apparatus was replaced by an evacuated 1500 c.c. flask containing a measured quantity of standardised baryta. To prevent a too great pressure being developed in the apparatus, a T-piece was inserted in the oxygen inlet tube with its end dipping in several cm. of water, and the current of oxygen regulated to cause a gentle stream of bubbles. When the sulphuric acid was added to the reaction vessel, containing the weighed substance with chromic acid and full of oxygen, the tap of the evacuated flask was turned slightly to suck in the acid. About two hours were sufficient for an estimation. The baryta, after being gently shaken occasionally towards the end of the operation, was titrated in the flask with $N/20$-hydrochloric acid. The difference between this value and that obtained in a blank experiment under the same conditions is a measure of the carbon dioxide. The results are given in Table II. With N/20-acid, 0·1 c.c. = 0·00003 gram of carbon, and under the experimental conditions the titrations probably have this accuracy, which is greater than it is possible to obtain by weighing the carbon dioxide.

TABLE II.

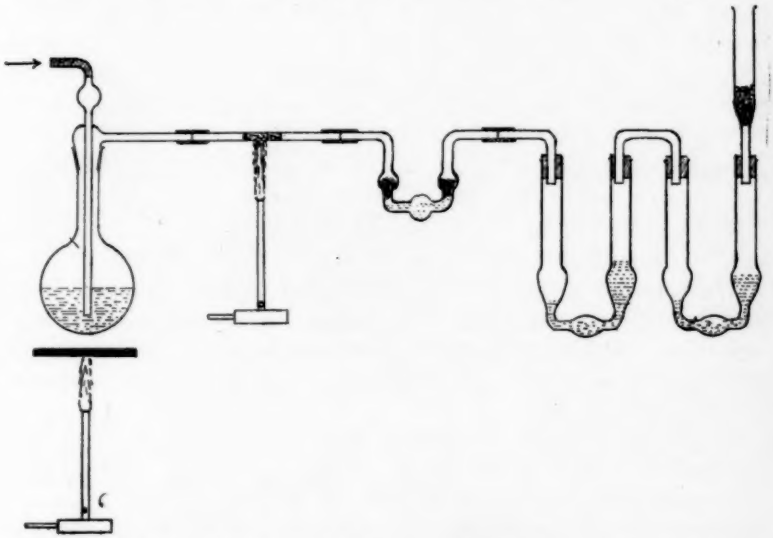
Substance.	Weight.	C.c $N/20$-$Ba(OH)_2$.	Found per cent.	Calc. per cent.
Sucrose	0·0282	39·3	41·8	42·2
	0·0208	28·3	42·3	
Catechol.....	0·0171	36·85	64·6	65·5
	0·0162	35·3	65·2	
Resorcinol	0·0170	36·8	64·9	65·5
	0·0147	31·95	65·1	

There is, then, evidence that the chromic acid method can be used for almost all compounds, although it has no advantages over the ordinary combustion methods, except in the rare instances when the compound is explosive or burnt with great difficulty. It might be of use, however, in the case of compounds, for which an accurate value is required to establish the formula, to confirm the numbers obtained otherwise. It can also be employed when only a very small quantity of the substance is available. Preliminary experiments, in which baryta in an exhausted flask was used to absorb the carbon dioxide, have been made to estimate carbon in steel, and also small quantities of organic matter in

solution, such as might be obtained in experiments on plant physiology. Thus 10 c.c. of a sugar solution containing 0·0106 gram, after having been evaporated to dryness in the reaction vessel, gave on subsequent treatment with the oxidising mixture carbon dioxide corresponding with 0·0104 gram of sugar.

Estimation of Carbon and Bromine.

The substance is weighed out into the reaction vessel (see figure) and chromic acid is added; the stopper, lubricated with syrupy phosphoric acid, is inserted, and a stream of oxygen (free from carbon dioxide) is passed for several minutes to expel the air. To the first absorption tube 10 c.c. of sodium hydroxide (approxi-



mately 1·3*N*) and 2 c.c. of 2*N*-sodium sulphite (to convert hypobromite into bromide) are added, and to the second absorption tube 10 c.c. of sodium hydroxide, part of which is retained by the glass beads of the exit tube. Redistilled sulphuric acid (25—30 c.c.) is now poured through a funnel into the reaction vessel, and a stream of oxygen is passed through the apparatus at such a rate as to cause a group of bubbles in the absorption tubes every two or three seconds. If the reaction has not begun, heat is applied at first gently, and afterwards a little more strongly. When the initial violence of the gas evolution has subsided, the apparatus may be left without attention, and in eighty to ninety minutes the operation is finished. The contents of the two absorption tubes are washed into a flask, heated to boiling, and then

treated with about 5 c.c. of hot saturated barium nitrate solution. The liquid is filtered, and the alkali in the filtrate is titrated with $N/3$-nitric acid, phenolphthalein being used as indicator. The difference between this titre and that obtained under the same conditions with no substance present gives a measure of the carbon dioxide and bromine. The solution is now rendered more strongly acid with nitric acid, 10 c.c. of $N/10$-silver nitrate are added, and the excess of silver found with $N/10$-ammonium thiocyanate. The silver nitrate should have been standardised under exactly the same conditions with pure potassium bromide, whereby the error of the pipette and that due to traces of chloride in the reagents are eliminated (compare T., 1915, **107**, 905). The value for the bromine, reduced to $N/3$, is subtracted from the total titre to obtain the value for the carbon dioxide. As in this operation a smaller number is subtracted from a much larger one, the error due to the fact that this is a difference method is almost inappreciable. To show the method of calculation, the following example for tetrabromodiphenol will suffice:

0·1241 required 20·85 c.c. $N/3$-HNO_3, 9·85 c.c. $N/10$-$AgNO_3$ (Br = 63·5); 9·85 c.c. $N/10 = 2·95$ c.c. $N/3$.

$20·85 - 2·95 = 17·90$ c.c. $N/3$-HNO_3 (C = 28·9).

$C_{12}H_6O_2Br_4$ requires C = 28·7; Br = 63·8 per cent.

The time for a complete analysis is not longer than two hours, and during more than half of that time the apparatus requires no attention. In Table III are the numbers obtained for various compounds; the calculated percentage values are included in brackets.

TABLE III.

Substance.	Weight.	HNO_3, c.c. $N/3$.	$AgHNO_3$, c.c. $N/10$.	Carbon, per cent.	Bromine, per cent.
Bromonaphthalene ...	0·1121	33·94	5·4	57·6 (58·0)	38·6 (38·6)
Dibromocresol	0·1190	21·59	8·95	31·8 (31·6)	60·3 (60·4)
Tribromophenol	0·1010	13·82	9·15	22·0 (21·8)	72·5 (72·5)
Tetrabromodiphenol..	0·1241	20·85	9·85	28·9 (28·7)	63·5 (63·8)
Tribromomethylquinone	0·1167	16·71	9·7	23·7 (23·4)	66·6 (66·8)
Tribromoaniline	0·1061	14·46	9·7	21·7 (21·8)	73·0 (72·7)
Acetobromotoluidide..	0·0969	24·14	4·3	47·5 (47·4)	35·4 (35·1)
Caprotribromoanilide.	0·1121	21·10	7·9	33·4 (33·6)	56·3 (56·0)
Bromonitrobenzene...	0·1096	21·04	5·4	35·5 (35·7)	39·4 (39·6)
Dibromonitrocresol...	0·1256	19·34	8·15	26·9 (27·0)	51·9 (51·5)

Estimation of Carbon and Chlorine.

The procedure is as for bromo-compounds, except that between the small U-tube containing chromic and sulphuric acids and the first absorption tube must be inserted a second short length of silica tubing, which is likewise heated. By this means, the chromyl

chloride formed by the action of the chlorine on the chromic acid in the small U-tube is decomposed, with the deposition of chromic oxide. This precaution is necessary, as chromyl chloride is capable of neutralising twice as much alkali as the corresponding amount of chlorine. Actually a trace of chromyl chloride is sometimes carried into the alkali, to which it imparts a faint yellow colour, but in too small an amount to introduce an error. It is also to be noticed that a faint smoke of finely divided chromic oxide, formed chiefly by the decomposition in the first silica tube of the chromyl chloride from the reacting mixture, is carried through the apparatus without absorption. The results obtained for chloro-compounds were as satisfactory as in the bromine and carbon estimations; the numbers for several substances are given in Table IV.

TABLE IV.

Substance.	Weight.	HNO_3, c.c. $N/_3$.	$AgNO_3$, c.c. $N/10$.	Carbon, per cent.	Chlorine per cent.
Dichlorodiphenol	0·0796	24·59	6·35	57·0 (56·5)	28·3 (27·8)
,, ...	0·0830	25·44	6·45	56·7	27·6
Dichlorohydroxytoluic acid	0·0992	24·36	9·05	43·7 (43·5)	32·4 (32·2)
	0·1017	25·02	9·2	43·8	32·2
Dichloronitrocresol ...	0·0836	18·20	7·5	33·2 (37·9)	31·9 (32·0)
,, ...	0·0934	20·08	8·3	37·6	31·6

Nitrogen, Carbon, and Halogen.

According to Fritsch (*Annalen*, 1896, **292**, 83), it is possible not only to estimate carbon by the chromic acid method, but also nitrogen when attached to a carbon atom. In compounds of this nature, the nitrogen remains behind in the acid mixture in the form of an ammonium salt, and its amount may be found by distillation with alkali. A means would thus seem available to estimate nitrogen, carbon, and halogen in a single operation. Experiments, however, showed that the results obtained for nitrogen were invariably low. Thus for tribromoaniline, values varying between 2·8 and 4·1 per cent., instead of the theoretical 4·3 per cent., were obtained; similar results were found for other compounds also, and it was further noticed that the divergence increased with the temperature to which the reaction mixture was raised. It was also discovered that ammonium salts, on being heated with chromic and sulphuric acids, showed on subsequent distillation with alkali a loss of ammonia. It would seem, therefore, that the chromic acid modification of the Kjeldahl method is not altogether satisfactory.

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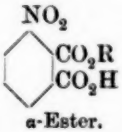
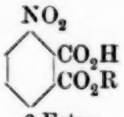
XXVI.—*The Relation of Position Isomerism to Optical Activity. Part X. The Menthyl Alkyl Esters of Phthalic Acid and its Nitro-derivatives.*

By JULIUS BEREND COHEN, DAVID WOODROFFE, and LEONARD ANDERSON.

ACCORDING to Victor Meyer's esterification law, 3-nitrophthalic acid should yield the β-acid ester, and neither the α-acid nor neutral ester:



α-Ester.



β-Ester.

Wegscheider and Lipschitz (*Monatsh.*, 1900, **21**, 781) have stated that in the absence of mineral acids, by using the anhydride or by the action of methyl iodide on the potassium hydrogen salt, the α-ester is obtained. whereas the β-ester is produced by Fischer and Speier's method. Similar observations were made by Marckwald and McKenzie (*Ber.*, 1901, **34**, 485), who found that when 3-nitrophthalic acid was esterified with *iso*butyl and *sec.*-butyl carbinols by the Fischer-Speier method the main product was the β-ester, but that the α- and normal esters were also present, whereas by using the anhydride the main product was the α-ester together with a small quantity of the β-ester. Subsequently McKenzie (T., 1901, **79**, 1135) showed that on esterifying 3-nitrophthalic anhydride with methyl alcohol a mixture of α- and β-ester was formed, from which the pure α-compound was isolated (m. p. 152—153°). He also esterified the acid by the Fischer-Speier method, and obtained a mixture of the two esters which were not separated. Using the latter method with methyl alcohol and hydrogen chloride as catalyst we found in one experiment that 10 grams of 3-nitrophthalic acid yielded 7 grams of nearly pure β-methyl ester (m. p. 161—163°) or 65 per cent. With the anhydride 71 per cent. of crude α-ester (m. p. 148—152°) was obtained, or 50 per cent. of the purified ester (m. p. 152—153°). Very similar results were obtained with ethyl, propyl, and *iso*butyl alcohols, that is to say, the Fischer-Speier method gave in each case a preponderating quantity of β-ester, whilst the anhydride yielded an excess of the α-compound.

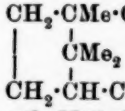
The following are the melting points of the two series of esters prepared in this way:

Alkyl group.	α-Ester.	β-Ester.
Methyl	152—153°	164°
Ethyl.....	156—157	112
Propyl	138—139	122—123
*iso*Butyl	176—177	149
*iso*Amyl	165—166	95
sec. Butylcarbinyl.....	156—158	113—114
Benzyl	174	165
Menthyl *	160—162	—

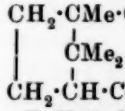
* The β-menthyl ester could not be obtained by the direct action of the alcohol on the acid, nor could it be prepared by the half hydrolysis of the α-methyl, β-menthyl ester, as in this case it is always the β-ester group which is first hydrolysed.

In order to examine the effect of groups other than the nitro-group in determining the formation of one or other of the isomeric esters, we had recourse to camphoric acid, which contains positive alkyl groups adjoining the carboxyl groups and bromosuccinic acid with a halogen atom in a similar position, in default of a 3-alkyl- or 3-halogen-phthalic acid, which are difficult to obtain.

In the case of camphoric acid the anhydride has little or no action on the alcohols, whilst the action of sodium alkyloxide on the anhydride gives the same product as that obtained by the action of sulphuric acid on a mixture of the alcohol and camphoric acid, namely, the *ortho*-alkyl ester (Walker, T., 1892, **61**, 1090; 1893, **63**, 498; Aschan, *Ber.*, 1894, **27**, 2001; Haller, *Compt. rend.*, 1892, **114**, 156). The isomeric *allo*-alkyl ester can only be obtained by the half-hydrolysis of the neutral ester:



ortho-Methyl ester.



allo-Methyl ester.

The influence of the alkyl groups is therefore quite unlike that of the nitro-group in phthalic acid, and may be explained by the weakening effect of the positive alkyl groups on the negative character of the neighbouring carboxyl group, which is greater in the *allo*- than the *ortho*-position. The monalkyl esters of monobromosuccinic acid were prepared, the one by treating the acid with the alcohol in presence of hydrogen chloride and the other by the action of the alcohol on the anhydride. The two substances were liquids which could not be solidified by cooling nor distilled without decomposition, and were therefore not distinguishable in the ordinary way. After some attempts to prepare solid derivatives we eventually succeeded in differentiating them by converting them into the menthyl esters and finding their rotation constants. As these were different it may be assumed that the two esters were

different or mixtures in different proportions; but it left unanswered the question as to which was which. From analogy to the nitrophthalic esters, the acid ester obtained from the anhydride should have the ester group nearest to the bromine atom, whilst that obtained by the Fischer-Speier method should be represented by the one with the more distant ester group. Now it has been shown (Cohen, T., 1914, **105**, 1892) that in benzene derivatives the effect of a halogen in proximity to a menthyl ester group lowers the rotation. If this is the case with the bromosuccinic esters, that obtained from the anhydride should have the higher rotation, a conclusion which is contrary to our observation:

$CHBr\cdot CO_2Me$	$CHBr\cdot CO_2\cdot C_{10}H_{19}$
$CH_2\cdot CO_2\cdot C_{10}H_{19}$	$CH_2\cdot CO_2Me$
$[M]_D^{20}$ $-161°$.	$[M]_D^{20}$ $-171°$.
(From anhydride).	(From acid.)

The further question may be raised as to whether an assumption drawn from the analogy of certain substituted benzoic esters is justified in the present case; for we are as yet ignorant of the effect of an adjoining ester group on the rotation of an active ester group. Considerations of this nature have led us to study the effect of substitution on the menthyl alkyl esters of a series of dibasic acids of known constitution.

The first substances examined were the methyl menthyl esters of camphoric acid. Although they cannot be regarded as pointing to any very definite conclusion, as the activity is dependent on both acid and menthyl group of opposite rotations and is further complicated by the presence of two dissimilar asymmetric carbon atoms in the acid radicle, the rotation constants have a certain interest and are as follows:

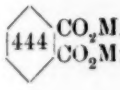
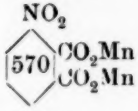
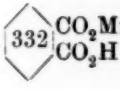
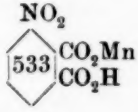
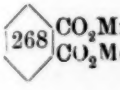
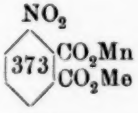
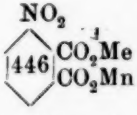
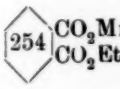
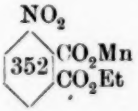
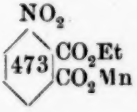
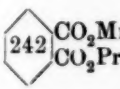
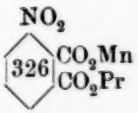
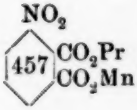
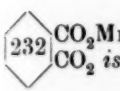
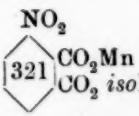
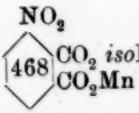
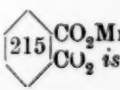
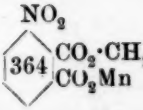
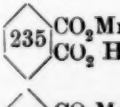
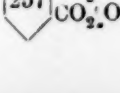
Camphoric Esters.

$CH_2\cdot CMe\cdot CO_2\cdot C_{10}H_{19}$	$CH_2\cdot CMe\cdot CO_2Me$
$\vert \quad CMe_2$	$\vert \quad CMe_2$
$CH_2\cdot CH\cdot CO_2Me$	$CH_2\cdot CH\cdot CO_2\cdot C_{10}H_{19}$
allo-Menthyl *ortho*-methyl.	*allo*-Methyl *ortho*-menthyl.
$[M]_D^{20}$ $-70{\cdot}8°$.	$[M]_D^{20}$ $-87{\cdot}9°$.

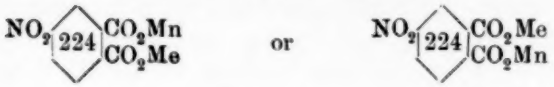
If we deduct from these values the constants for *ortho*-methyl camphoric ester, $[M]_D$ $+110{\cdot}3°$, and *allo*-methyl camphoric ester, $[M]_D$ $+93{\cdot}2°$ (Haller, *Compt. rend.*, 1892, **114**, 1516) we obtain the same number, namely, 181·1, from which it may be inferred that the menthyl group has the same value in both esters. If, on the other hand, we deduct the value for camphoric acid, $[M]_D$ $+97{\cdot}8°$, from that of the *allo*-menthyl acid ester, $[M]_D$ $-89{\cdot}4°$, we obtain a

higher value than either of the above. It is clear, therefore, that the alkyl ester group in this position tends to lower the value of the adjoining menthyl ester group more than the free carboxyl group.

This effect on the rotation is much more marked in the case of the phthalic and nitrophthalic menthyl esters, the rotations of which are given in the following table (Mn = menthyl), the molecular rotations (lævogyrate) being printed in round figures within the hexagon:

I. *Alkyl Menthyl Phthalate.*	II. *β-Alkyl α-Menthyl 3-Nitrophthalate.*	III. *α-Alkyl β-Menthyl 3-Nitrophthalate.*
		—
		—
		
		
		
		
	—	
	—	—
	—	—

Alkyl Menthyl 4-Nitrophthalate.



In reviewing the above results it will be noticed that the presence of an alkyl ester group adjoining the menthyl ester group lowers the rotation. This is best seen in columns I and II by comparing the rotations of hydrogen menthyl phthalate and nitrophthalate with those of the alkyl menthyl esters of the same series. In the second place it will be observed in the two series just referred to, that with the increase in the size of the alkyl group, the rotation is diminished (in the case of the phthalic esters the rotation rises again after the *iso*amyl group has been passed). A similar phenomenon has been noted in the case of the esters of camphoric acid (Brühl and Braunschweig, *Ber.*, 1892, **25**, 1796):

Camphoric ester.	$[M]_D$.
Dimethyl	109·9
ortho-Methyl, *allo*-ethyl	110·1
ortho-Ethyl, *allo*-methyl	93·0
Diethyl	92·9

It appears from this table that the alkyl group in the *allo*-position has no influence on the rotation; for the dimethyl and *ortho*-methyl and the diethyl and *ortho*-ethyl compounds have almost identical values.

That the *ortho*-group or its equivalent, that is, the meta-position in the benzene ring, possesses the dominating influence in raising the rotation is most strikingly emphasised in the esters of column III, where the rotations (with the exception of that of the benzyl derivative) are not only higher than those of the corresponding isomerides, but are actually enhanced by the larger radical attached to the interposed ester group.

At the bottom of the table is introduced the rotation of the menthyl methyl ester of 4-nitrophthalic acid. We have so far failed to obtain either the hydrogen menthyl or dimenthyl esters of this acid or to determine which of the two alternative formulæ is correct. On heating 4-nitrophthalic anhydride for several hours to 110—120° with one or two molecular proportions of menthol a glassy mass was obtained in both cases, no portion of which dissolved in sodium carbonate, and when distilled in a current of steam gave very little free menthol where one molecular equivalent was used, but lost about half the original quantity where two equivalents were added. The product dissolves completely in water, alcohol, and ether, and could not be crystallised, but is readily

decomposed by sodium hydroxide, liberating menthol. In order to determine the structure of the menthyl methyl ester, the acid methyl ester was distilled with lime, which should yield the methyl ester of nitrobenzoic acid of known structure, but the experiment, which was repeated several times, failed to give a satisfactory result.

Although these data are not available, it is interesting to note that the removal of the nitro-group from the immediate vicinity of either ester group lowers the rotatory value to the order of the unsubstituted esters in column I. Moreover, it may be safely inferred that the monomenthyl and dimenthyl esters of this acid will have a lower rotation than the corresponding esters of 3-nitrophthalic acid.

The following is a brief summary of the results:

(1) The general effect of the nitro-group is to raise the rotation of the active ester group in its vicinity, as observed in the case of the nitrobenzoic esters (Cohen and Armes, T., 1905, **87**, 1190).

(2) In 3-nitrophthalic ester the active ester group in the meta-position with respect to the nitro-group has a higher rotation than that in the ortho-position, or, in other words, the interposition of an inactive ester group increases the rotation of the active group.

(3) The effect of the alkyl ester group is to diminish the rotation of the adjoining active ester group, and with increase in length of the carbon chain in the alkyl group up to five carbon atoms the rotation decreases, after which it increases (columns I and II). If, however, the alkyl ester group intervenes between the nitro- and active ester group, the tendency is the reverse, namely, to increase the rotation with increase in the length of the chain.

(4) The free carboxyl group appears to raise rather than lower the rotation of the adjoining active ester group, and in this respect resembles the nitro-group. The following comparison exhibits this effect:

Menthyl benzoate.	*o*-Nitromenthyl benzoate.	Hydrogen menthyl phthalate.
[M] −239°	−381°	−332°

Experimental.

Camphoric Methyl Menthyl Esters.

ortho-*Methyl* allo-*Menthyl Camphorate*.—The *ortho*-methyl ester was prepared by Walker's method (*loc. cit.*), and melted at 75—77°. Five grams were heated with an equal weight of phosphorus pentachloride, and the phosphoryl chloride was removed in a vacuum on the water-bath, dry air being slowly passed through at the end of the operation. The acid chloride, which is liquid, was then heated

with rather more than one equivalent of menthol. The reaction began at 95—100°, and was complete after one and a-half hours at 115—120°. The product was distilled in a current of steam until all the free menthol was removed, extracted with ether, the free acid separated with sodium carbonate solution, the ethereal solution dehydrated, and the ether removed by distillation and subsequently heating in a vacuum on the water-bath. The yield of ester was 7·5 grams. It is a colourless, viscid liquid, which does not crystallise on keeping. It can be distilled without change of rotation under diminished pressure and boils at 203—205°/5 mm.:

0·1565 gave 0·4098 CO_2 and 0·1412 H_2O. C = 71·47; H = 10·02.
$C_{21}H_{36}O_4$ requires C = 71·59; H = 10·22 per cent.

Specimen I (not distilled).	Specimen II (distilled).	Specimen II (not distilled).	Mean.
α_D^{20} −6·12°	−6·03°	−6·28°	−6·20°
α_D^{100} −6·03	—	−6·30	−6·17

Specimen I: D^{20} 1·020; D^{100} 0·9656; $l = 3·02$ cm.
$[\alpha]_D^{20}$ −20·1°; $[\alpha]_D^{100}$ −21·1°.
$[M]_D^{20}$ −70·8°; $[M]_D$ −74·4°.

allo-*Methyl* ortho-*Menthyl Camphorate*.—The *allo*-methyl ester was prepared as described by Walker by half-hydrolysis of the neutral methyl ester. From 10 grams of anhydride, 7 grams of *allo*-methyl ester were obtained (m. p. 84—86°). The menthyl ester was prepared as described above. The action of the menthol on the acid chloride began at about 80°:

0·160 gave 0·4187 CO_2 and 0·1432 H_2O. C = 71·37; H = 9·94.
$C_{21}H_{36}O_4$ requires C = 71·59; H = 10·22 per cent.

α_D^{20} −7·71°; α_D^{100} −7·66°.
D_4^{20} 1·021; D_4^{100} 0·9629; $l = 3·02$ cm.
$[\alpha]_D^{20}$ −25°; $[\alpha]_D^{100}$ −26·3°.
$[M]_D^{20}$ −87·9°; $[M]_D^{100}$ −92·7°.

allo-*Menthyl Hydrogen Camphorate*.—Five grams of *ortho*-methyl *allo*-menthyl ester were hydrolysed with alcoholic potassium hydroxide containing 0·8 gram of alkali. The alcohol was evaporated, and the product extracted with ether to remove unhydrolysed ester. The residue was acidified and again extracted with ether. After removing the ether, 1·5 grams of viscid liquid remained, which solidified, and after crystallisation from light petroleum melted at 101°:

0·5011 gram in 50 c.c. benzene in a 2-dcm. tube gave α 0·53°;
$[\alpha]_D^{20}$ −26·45°; $[M]_D^{20}$ −89·4°.

ortho-*Menthyl hydrogen camphorate* was prepared as just

described from the corresponding methyl menthyl ester, which, however, is much more difficult to hydrolyse, requiring long boiling with excess of alcoholic potash. It crystallises from dilute methyl alcohol in colourless needles which melt at 105—107°:

0·3917 gram in 25 c.c. of benzene in a 2-dcm. tube gave 0·52°:
$[\alpha]_D^{20}$ −16·6°; $[M]_D^{20}$ −56·1°.

Bromosuccinic Methyl Menthyl Esters.

The bromosuccinic acid was prepared by the Hell-Volhard method (Volhard, *Annalen*, 1887, **242**, 141), in which bromosuccinyl bromide is made and decomposed by water. The best results were obtained by dropping the crude bromide into twice the weight of water at 60—70° and stirring. At a lower temperature the decomposition proceeds very slowly, and if the water is boiled as recommended by Volhard the product is completely converted into fumaric acid.

After conversion of the acid bromide into acid the aqueous portion is extracted several times with ether, the latter dehydrated over calcium chloride, and the ether partly removed on the water-bath. The remainder is left to evaporate at the ordinary temperature or further concentrated under diminished pressure. In one preparation 80 grams of succinic anhydride yielded 267 grams of bromide, which gave 142 grams of crude bromosuccinic acid, or 90 per cent. of the theoretical amount. The acid was purified by dissolving it in the smallest quantity of ether and then adding an equal volume of light petroleum. After three crystallisations the acid melted at 160—161°. The best method of preparing the anhydride of the bromosuccinic acid is to heat the latter with twice its weight of acetyl chloride in a sealed tube at 100° for three to four hours. The product is then fractionated under diminished pressure and the portion boiling at 130°/5—6 mm. collected. Twenty grams of acid yielded 12·5 grams of pure anhydride, or 70 per cent. of the theoretical. It is a colourless, viscid liquid which does not solidify at 0°.

α-Methyl hydrogen bromosuccinate was prepared by adding to the anhydride the equivalent of one molecule of methyl alcohol and shaking. Heat was evolved and the mixture became clear and viscid. The product dissolves completely in water, from which it may be separated by saturating with salt and dissolving in benzene. The benzene solution was dehydrated with anhydrous sodium sulphate and the benzene removed on the water-bath and finally in a vacuum.

α-Methyl β-Menthyl Bromosuccinate.—The acid ester was dissolved in a little benzene and an equal weight of phosphorus penta-

chloride added. After the reaction was complete the benzene and phosphoryl chloride were removed by distilling on the water-bath under diminished pressure. The calculated quantity of menthol was then added and the mixture heated in the oil-bath to 110—120° until no more hydrogen chloride was evolved. The product was then distilled in a current of steam to remove free menthol and the residue shaken with sodium carbonate solution to dissolve any free acid. The ethereal extract was dehydrated and the ether removed in the usual way. From 12·5 grams of anhydride, 14 grams of acid ester and 21 grams of methyl menthyl ester were obtained. The ester prepared in this way is a pale yellow, viscid liquid:

0·2198 gave 0·1173 AgBr. Br = 22·72.

$C_{15}H_{25}O_4Br$ requires Br = 22·92 per cent.

α_D^{20} −16·85°; D_4^{20} 1·210; l = 3·02 cm.

$[\alpha]_D^{20}$ −46·1°; $[M]_D^{20}$ −161°.

β-Methyl Hydrogen Bromosuccinate.—The bromosuccinic acid was mixed with the calculated amount of methyl alcohol saturated with hydrogen chloride and the mixture heated at 70—80° for two to three hours. The product was diluted with a little water and filtered from a small quantity of undissolved fumaric acid. It was separated from the neutral ester by shaking with sodium carbonate, in which the neutral ester is insoluble. The aqueous portion was slightly acidified with hydrochloric acid, the solution saturated with salt and extracted with benzene. The final treatment is the same as described above. From 15 grams of acid 5 grams of the monomethyl ester were obtained. It is a pale yellow, viscid liquid closely resembling the α-methyl ester.

β-Methyl α-Menthyl Bromosuccinate.—The acid methyl ester was converted into the menthyl ester in the manner previously described and had the same appearance as the corresponding α-methyl-β-menthyl ester. From 5 grams of the methyl ester nearly 8 grams of the methyl menthyl ester were prepared:

0·2310 gave 0·1222 AgBr. Br = 22·60.

$C_{15}H_{25}O_4Br$ requires Br = 22·92 per cent.

α_D^{20} −17·52°; D_4^{20} 1·181; l = 3·02 cm.

$[\alpha]_D^{20}$ −49·1°; $[M]_D^{20}$ −171°.

The Alkyl Menthyl Esters of Phthalic Acid.

The method employed in the preparation of all these esters may be illustrated in the case of methyl menthyl phthalate. Twenty-five grams of phthalic anhydride and 60 grams of methyl alcohol were boiled under reflux for two hours. The excess of methyl alcohol was removed on the water-bath and finally under diminished pres-

sure in a current of air. The residue solidified, and after crystallisation from benzene melted at 82·5°. The yield was equal to the weight of anhydride taken. Five grams were dissolved in 50 c.c. of dry benzene, 5·8 grams of phosphorus pentachloride added, and the mixture was heated on the water-bath until hydrogen chloride ceased to be evolved. The benzene and phosphoryl chloride were removed by heating on the water-bath under diminished pressure. To the residue 4·6 grams of menthol were added, and the whole was heated to 100—110° for an hour, when the reaction was complete. The excess of menthol was then removed by distillation in a current of steam, the residue shaken with sodium carbonate solution, dehydrated with calcium chloride, and the ether removed, first on the water-bath and then by heating under diminished pressure. The ethyl, propyl *iso*butyl, *iso*amyl, and octyl esters were prepared in the same way. With increase in molecular weight of the alcohol the combination with the anhydride proceeded less readily. On the other hand, if the temperature were raised above 100° some neutral ester was also formed. The *iso*amyl alcohol used in the preparation was obtained from *iso*amyl chloride by treatment of fusel oil as described by Le Bel, and was almost free from the active isomeride. In the case of hexyl alcohol the amount of acid ester formed at the temperature of the water-bath was so small, whilst at 120° only the neutral ester was obtained, that it had to be prepared finally by the half hydrolysis of the neutral ester.

The excess of alcohol used in the preparation of the acid esters of the higher alcohols was removed either by distillation in a current of steam or under diminished pressure, as the temperature at which the alcohol distilled produced decomposition of the ester. The acid chlorides and menthyl alkyl esters were all obtained in the manner already described.

It was observed that the temperature at which the reaction began between acid chloride and menthol rose with the molecular weight of the alcohol. The products were all colourless, viscid liquids, and the rotations were all determined with the pure substances without solvent in a tube 3·02 cm. in length.

Alkyl menthyl phthalate.	α.	D.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
Methyl	26·99°	1·0691°	83·62°	265·1
Ethyl	24·24	1·0555	76·03	252·4
Propyl.....	21·93	1·0447	64·49	240·6
*iso*Butyl	19·97	1·0338	63·96	30·2
*iso*Amyl	17·25	1·0215	55·90	209·0
Hexyl	18·29	1·0179	60·26	233·7
Octyl	18·71	1·0095	61·38	255·4

The following results were obtained on analysis:

Alkyl menthyl ester.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Methyl	71·68	8·23	71·69	8·17
Ethyl.....	72·19	8·23	72·30	8·43
Propyl	72·90	8·60	72·83	8·67
*iso*Butyl	73·43	8·81	73·33	8·89
*iso*Amyl	73·58	8·95	73·79	9·09
Hexyl	73·99	9·22	74·23	9·28

Acid and Neutral Menthyl Esters of Phthalic Acid.

The acid and neutral menthyl phthalates were first prepared by Arth (*Ann. chim. Phys.*, 1886, [vi], **7**, 485) by heating the calculated quantities of anhydride and menthol for thirty-six hours at 110° in the first case and for forty hours at 135—140° in the second. We have repeated these preparations, and find that both melting points and specific rotations differ from those given by Arth. According to this observer, the acid phthalate melts at 110° and has $[\alpha]_D^{20}$ −105·55°, and the neutral phthalate melts at 133° and has $[\alpha]_D^{20}$ −94·72° in benzene, whilst we find for the former m. p. 111—112° and $[\alpha]_D^{20}$ −109·32°, and for the latter m. p. 99° and $[\alpha]_D^{20}$ −100·5° in benzene.

Alkyl and Alkyl Menthyl Esters of 3-Nitrophthalic Acid.

The nitrophthalic acid used in these preparations was obtained by the following slight modification of the usual method (Miller, *Annalen*, 1881, **208**, 224): 150 grams of phthalic anhydride are placed in a round flask of 1 litre capacity, and a mixture of 225 grams of concentrated sulphuric acid and 225 grams of fuming nitric acid (D rather above 1·5) is added. The contents of the flask are well mixed in the fume cupboard. As soon as bubbles of gas appear the flask is immersed in ice and water to moderate the reaction, which becomes very violent. When the reaction has subsided the flask is heated on the water-bath for two hours and the contents poured into 300 c.c. of water. The mixture is filtered after some time and the precipitate drained. The product, which consists of two isomerides, is crystallised three times from water, when about 60 grams of nearly pure 3-nitrophthalic acid (m. p. 215°) are obtained. The mother liquors contain 4-nitrophthalic acid, which crystallises out on evaporation. A better separation than the above is effected by converting the whole of the product into the ethyl ester by the Fischer-Speier method. The 3-nitro-acid forms only the acid ester, and may be removed by shaking the product with sodium carbonate, whilst the neutral ester of 4-nitrophthalic acid remains undissolved. The two acids separated in this way may then be regained by hydrolysis of the esters. The anhydrides of

both acids were obtained by heating to boiling for a short time with an equal weight of acetic anhydride until a clear solution is obtained. The excess of acetic anhydride and acetic acid is then removed by evaporation on the water-bath, and the residue crystallised from benzene or a mixture of benzene and light petroleum. The anhydride of the 3-nitro-acid melts at 161—162°, that of the 4-nitro-acid at 119—120° (not at 114° as given in Beilstein).

The method for preparing the α- and β-acid alkyl esters has already been described. They gave the following results on analysis. Those that have already been prepared and examined by other observers are omitted.

Acid alkyl ester.	Carbon.		Hydrogen.	
	Found.	Calculated.	Found.	Calculated.
α-Ethyl	50·00	50·20	3·69	3·76
β-Ethyl	50·05	50·20	3·70	3·76
α-Propyl	52·24	52·18	4·21	4·35
β-Propyl	52·07	52·18	4·19	4·35
α-*iso*Butyl.....	53·71	53·94	4·80	4·87
β-*iso*Butyl	53·86	53·94	4·76	4·87
α-Menthyl.....	61·71	61·90	6·40	6·59

The conversion into the acid chlorides and alkyl menthyl esters may be illustrated in the case of α- and β-methyl menthyl esters. Whereas the β-acid esters may be converted into the chloride by the use of phosphorus pentachloride without solvent, a purer product is obtained from the α-acid ester by using thionyl chloride. Five grams of α-methyl ester and 10 grams of thionyl chloride were heated on the water-bath until a clear solution was obtained; excess of thionyl chloride was removed on the water-bath under diminished pressure, and finally a current of dry air was drawn through the liquid. On cooling, the acid chloride was crystallised from benzene and light petroleum. The product was heated with a slight excess of menthol for two to three hours at 110—120°, when hydrogen chloride ceased to be evolved. The reaction was usually observed to begin at 95—100°. The ester was purified in the usual way by removing free menthol in steam, and the free acid ester by shaking the ethereal solution with sodium carbonate. The ethereal solution was dehydrated and the ether removed first on the water-bath and finally under diminished pressure in a current of dry air.

The following table gives the melting points of the ester chloride and alkyl menthyl esters:

Acid alkyl ester.	Ester chloride. m. p.	Alkyl menthyl ester. m. p.
α-Methyl	95—97°	66—67
β-Methyl	97—99	149—150
α-Ethyl	74—76	57—58
β-Ethyl	58—60	99
α-Propyl	32	38—40
β-Propyl	118	89
iso-Butyl	liquid	liquid
β-*iso*Butyl	liquid	76—77
α-Benzyl	74—75	—

It is interesting to note that the β-alkyl menthyl ester has a much higher melting point than the α-isomeride. The crystalline form of the two isomerides is also easily distinguished. Whilst the α-compounds crystallise in four-sided plates, the β-compounds form long prisms with pointed ends.

The α-benzyl β-menthyl ester was prepared from the β-acid methyl ester and converted into the acid chloride, which was heated with benzyl alcohol whereby the α-benzyl β-methyl ester is formed (m. p. 95°). By half hydrolysis the α-benzyl acid ester was obtained, which in turn was converted into the acid chloride and then heated with menthol. The β-compound cannot be prepared in this way, as by half-hydrolysis of the α-methyl β-benzyl ester the β-benzyl group is removed. The methyl menthyl ester of 4-nitrophthalic acid was prepared by heating the anhydride with excess of methyl alcohol.

The acid ester obtained in this way melted at 130—132°. It was converted into the acid chloride by heating with an equal weight of thionyl chloride. The clear, viscid liquid was heated with menthol and the product purified in the usual way. The methyl menthyl ester is a pale yellow liquid which showed no appearance of crystallisation.

The following are details of the polarimetric observations at 17—20°:

Alkyl menthyl ester of 3-nitrophthalic acid.	Weight in 100 c.c. of benzene.	α 2-dcm.	$[\alpha]_D$.	$[M]_D$.
α-Methyl	3·2224	−7·93	−122·9°	−446·4°
β-Methyl	2·9340	−6·03	−102·3	−373·4
α-Ethyl	2·3920	−6·00	−125·4	−472·9
β-Ethyl	2·7096	−5·06	−93·45	−352·1
α-Propyl	2·2228	−5·20	−116·9	−457·3
β-Propyl	2·5184	−4·20	−83·4	−326·0
α-*iso*Butyl	2·1396	−4·95	−115·7	−468·6
β-*iso*Butyl	2·3868	−3·78	−79·2	−320·7
α-Benzoyl	2·5912	−4·30	−83·0	−364·3
Methyl menthyl ester of 4-nitrophthalic acid	2·2304	−2·75	−61·6	−223·8

The rotation of the α-ethyl menthyl ester seems abnormally high, but a second preparation gave a similar result.

The following results were obtained on analysis of the α- and β-methyl and α-benzyl derivatives. It was not considered necessary to submit the other members of the series to analysis, seeing that the acid esters had been examined in this way:

	Carbon.		Hydrogen.	
Alkyl menthyl ester.	Found.	Calculated.	Found.	Calculated
α-Methyl β-menthyl	62·70	62·81	6·54	6·89
β-Methyl α-menthyl	62·41	62·81	6·46	6·89
α-Benzyl β-menthyl	60·67	60·95	4·24	4·13

In conclusion, we offer our thanks to Mr. H. Whitaker for his kindness in preparing for us the two methyl menthyl esters of bromosuccinic acid.

UNIVERSITY OF LEEDS. [*Received, January 25th*, 1916.]

XXVII.—*Compounds of Iron, Manganese, Lead and the Metals of Group II.*

By SPENCER UMFREVILLE PICKERING.

IN a previous communication (T., 1915, **107**, 942) it has been shown that cobalt and nickel form metallo-compounds analogous to those of copper; a similar examination is being made in the case of other metals, and the present communication deals with manganese, iron, lead, and all the elements of the periodic group II.

To establish the mere fact of the formation of such compounds, it has not been necessary to examine every case in detail; the existence of a metallo-compound may be first indicated by ascertaining whether alkalis react with an organic salt of the metal in question to form a soluble compound, instead of an insoluble basic salt, and then established by proving that the organic salts of the metal exist in two different forms, one a very sparingly soluble crystalline compound, the normal salt, the other a much more soluble salt of the same composition, non-crystalline, and generally obtained in the form of an emulsion, this soluble form changing spontaneously into the normal salt. The methods of preparation adopted were by (1) dissolving the hydroxide or carbonate in the acid, and precipitating by alcohol, the acids used

being tartaric, malic and citric; in some cases, also, racemic: (2) mixing solutions of the chloride, or other inorganic salt, of the metal with a potassium salt of the acid in question. Analysis of the product was not necessary in every case, since in many instances it had already been obtained and analysed by former investigators;* indeed, if the product of such reactions is found to contain no acid, no potassium, and no chlorine, it must necessarily consist either of the normal salt or of a substance differing from this only by the elements of water, and, as already pointed out (*loc. cit.*, p. 945), determining the water present leads to no useful results.

Action of Alkalis.

Those metallo-compounds, which corresponded with, and are convertible into, the normal salts, have been represented as being derived from the latter by the introduction of water into the molecule, and the union of the metal, which becomes quadrivalent, with one of the carbon atoms, as in I.

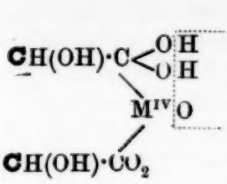
* Tartrates.—*Iron*, Dulk, *Annalen*, 1832, **2**, 62; Méhu, *Jahresber.*, 1873, 569. *Manganese*—Pfaff, *J. Chem. Phys.*, 1811, **4**, 377. *Lead*—Abegg, "*Handbuch d. anorg. Chem.*," Erdmann, *Annalen*, 1837, **21**, 14. *Magnesium*—Mayer, *Annalen*, 1857, **101**, 166; Dulk, *Annalen*, 1832, **2**, 59; Makovetzki, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 769; Johnsen, *Jahrb. Min.*, 1907, **23**, 246. *Zinc*—Zchiff, *Annalen*, 1863, **125**, 146; Frisch, *Jahresber.*, 1866, 400; Cantoni and Zachoder, *Bull, Soc. chim.*, 1905, [iii], **33**, 747; Werther, *J. pr. Chem.*, 1844, **32**, 385. *Cadmium*—Stromeyer, *Schw. J.*, 1818, **22**, 362. *Mercury*—Rose, *Ann. Phys. Chem.*, 1841, [ii], **53**, 127. *Calcium*—Cantoni and Zachoder, *loc. cit.*; Herz and Muhs, *Ber.*, 1903, **36**, 3716; Anschütz, *Annalen*, 1884, **226**, 197; Dulk, *J. Chem. Phys.*, 1832, **64**, 180, 193; Neumann, *ibid.*, p. 206; Eppler, *Zeitsch. Kryst. Min.*, 1899, **30**, 134. *Strontium*—Cantoni and Zachoder, *Bull. Soc. chim.*, 1904, [iii], **31**, 1122; Marignac, *Ann. Min.*, 1859, [v], **15**, 280; Dulk and Neumann, *J. Chem. Phys.*, 1832, **64**, 180, 193; Scacchi, *Ann. Phys. Chem.*, 1860, [ii], **109**, 373. *Barium*—Cantoni and Zachoder, *loc. cit.*; Hertz and Muhs., *loc. cit.*

Racemates.—*Iron* and *Manganese*. Fresenius, *Annalen*, 1842, **41**, 1.

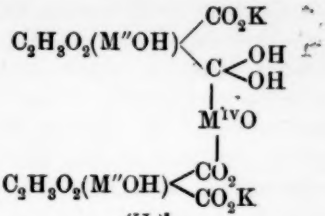
Malates.—*Iron*, Rosenthaler and Siebeck, *Arch. Pharm.*, 1908, **246**, 55. *Manganese*—Traube, *Zeitsch. Kryst. Min.*, 1899, **31**, 60. *Lead*—Otto, *Annalen*, 1863, **127**, 177. *Magnesium*—Traube, *loc. cit.*, p. 160; Hagen, *Annalen*, 1841, **38**, 265; Liebig, *Annalen*, 1833, **5**, 148. *Zinc*—Traube, *loc. cit.*, and *Jahrb. Min., Beil. Bd.*, 1898, **11**, 627; Liebig, *loc. cit.*; Hagen, *loc, cit.* *Calcium*—Traube, Liebig, and Hagen, *loc. cit.*; Iwig and Hecht. *Annalen*, 1886, **233**, 168. *Strontium*—Traube and Hagen, *loc. cit.* *Barium*—Liebig, *Annalen*, 1833, **5**, 149; 1838, **26**, 136.

Citrates—*Iron*, Heldt, *Annalen*, 1843, **47**, 157, Kämmerer, *Annalen*, 1868, **148**, 294; 1873, **170**, 176; Siboni, 1906, **1**, 65. *Manganese*—Heldt and Kämmerer, *loc. cit.*; Power, *Pharm. J.*, 1901, **13**, 135. *Lead, Magnesium, Zinc, Cadmium, Calcium, Strontium, Barium*, Helt and Kämmerer, *loc. cit.*

In many instances these investigations bear ample evidence, at any rate in the light of the present work, that the substance in question must exist in two different forms.



(I.)



(II.)

In that case, the action of potassium hydroxide should produce an analogous substance, with KHO instead of HHO, the alkali reacting with the organic salt in the proportions of K : M″; also, the compound produced should be slightly alkaline. Neither of these results obtained in the case of copper tartrate (T., 1911, **99**, 169); the proportion of alkali absorbed by the tartrate before any alkalinity appeared (and it appeared quite sharply) gave the ratio 4K : 3Cu, and the compound produced contained the metals in the ratio 2K : 3Cu, the equation for its formation being

$$3C_4H_4O_6Cu + 4KOH = (C_8H_4O_{12}Cu_2)CuK_2 + C_4H_4O_6K_2.$$

By the addition of alcohol this substance was precipitated; it differed considerably in physical properties from the more simple cupri-compounds, and the formula II was suggested for it.

It appears now, however, that the behaviour of copper is exceptional, in that the first stage of the reaction is suppressed, and that a secondary product alone is obtained. The results on adding alkali to seven other tartrates show that the ratio of alkali to metal is generally 1 : 1, and that the product, although neutral to phenolphthalein, is really slightly alkaline, as evidenced by its action on litmus, even when the addition of alkali does not exceed about 0·1 KOH : M″. The results, given below, show a mean of 0·99 : 1 for the ratio KOH : M″ on the first appearance of alkalinity towards phenolphthalein, manganese giving lower results, which are omitted. Such low results might be expected in some cases, owing to the slight alkalinity of the product.

Ratio of K : M *at Alkalinity to Phenolphthalein.*

	Tartrate.		Citrate.	
	First.	Full.	First.	Full.
Copper	1·34	1·34	1·92	1·02
Cobalt	1·00	1·09	—	—
Nickel	0·99	1·23	(0·24)	(0·89)
Manganese	(0·68)	1·07	0·72	0·98
Iron	0·99	1·34	0·90	0·93
Zinc	1·08	1·24	0·91	0·97
Cadmium	0·87	0·97	0·88	1·00
Lead	1·03	1·27	0·77	0·98
Mean	0·99	—	—	0·97

In all these cases, unlike that of copper, the initial alkalinity is not sharply marked, and increases only very gradually with further additions of alkali; full alkalinity is reached, so far as it is possible to judge, only with the proportions indicated in the second column. In four of the cases the latter values evidently approximate to that obtained with copper ($3M'' : 4K$), indicating the formation of the secondary product II. With cobalt, manganese and cadmium the reaction does not appear to proceed beyond the first stage. With cobalt, however, the second product has been isolated by digesting the tartrate with potassium hydroxide and precipitating with alcohol (*loc. cit.*, p. 952); it was also obtained in an impure condition in the case of nickel. Attempts to isolate it in the other cases have not been made.

Owing to the very sparing solubility of the tartrates themselves, the above determinations were made by taking solutions of an inorganic salt of the metal mixed with excess of potassium tartrate; from 4 to 12 equivalents of the latter were necessary to prevent the precipitation of a basic salt. With nickel, a steely-grey cloudiness appears just before alkalinity is reached; with cadmium and lead, a precipitate is formed, which redissolves some time before alkalinity is attained. In the case of iron, the liquid on the addition of alkali gradually becomes of a dark bottle-green colour, 500 to 1000 times more intense than that of iron as ferrous sulphate; with more alkali this colour disappears nearly entirely, but with still more alkali it reappears, being darker than before, the liquid gradually becoming opaque, and then suddenly forming a flocculent precipitate of greenish-black ferrous hydroxide. Time plays a conspicuous part in these changes; if excess of alkali is added in the first instance, a darkening of the liquid occurs, then a loss of colour, followed by a more intense darkening, and subsequent precipitation. These liquids if exposed to the air oxidise to form the brownish-yellow ferritartrate.

Solid ferrous tartrate or potassium ferrous tartrate treated with concentrated potassium or sodium hydroxide solution dissolves entirely to form a liquid which is nearly colourless at first, although it rapidly becomes green. After some time a dirty white, viscid solid separates, or can be precipitated at once by alcohol (T., 1913, **103**, 1366); whether this is the compound I or II has not been determined; it is very oxidisable, and on attempting to purify it by dissolving in water, and reprecipitating it with alcohol, it always decomposes. An analogous compound is obtained in the case of manganous tartrate, but it is still more unstable.

The colour changes in the case of the ferro-compounds are certainly obscure. In the communication referred to above, the

absence of colour in the freshly-prepared sodium ferrotartrate, and the fact that no iron anion appeared on the electrolysis of it, led to the conclusion that ferrous iron did not form ferro-compounds analogous to the cupri-compounds. This conclusion must be withdrawn, for on submitting to a stronger current a solution of the ferrotartrate which had become coloured, a green anion made its appearance in the gelatin tube; and, as regards colour-intensity, the great intensity exhibited by cupri-, ferri-, and cobalti-compounds has been found to be by no means an essential feature of metallo-compounds; this was proved by the results with nickel (T., 1915, **107**, 942), and is still more evident from the results detailed in the present communication.

Attempts to prepare the compound I were also made in the case of zinc and cadmium by adding potassium hydroxide to the zinci- and cadmicitrates and the cadmitartrate, and then precipitating by alcohol. Emulsions were obtained in both cases, but they were of such a gelatinous character that they could not be filtered or purified for analysis.

With mercury tartrate, potassium hydroxide gives a permanent precipitate of mercuric oxide; with the other metals of group II alkalinity, of course, appears at once.

An examination of the behaviour of the citrates with alkalis gave the results shown in the last two columns on p. 237. With copper, alkalinity to litmus and to phenolphthalein appeared at the same point; in the other cases it did not, and the alkalinity to phenolphthalein made its appearance before the ratio 1:1 was reached. The latter, however, is the ratio evidently attained when the alkalinity becomes full, there being, thus, no indication of the reaction proceeding to a second stage, as in the case of the tartrates. The appearance of alkalinity before the ratio 1:1 is reached, means that the primary compound is less stable than in the case of the tartrates. With the nickel compound this is conspicuously so; but the values here varied greatly, being dependent on dilution and on some factor which could not be determined. As the citrates contain three atoms of metal in the molecule, three compounds similar to I (p. 237) are possible. Owing to the colour of the solution, no determinations were possible in the case of a cobalt.

Although none of the metallo-compounds with potassium corresponding with I has been isolated, others containing the metal and potassium in the same ratio (1:1) have been obtained; these were the cupriracemates of sodium and potassium, the cupritartrates of sodium and lithium (T., 1912, **101**, 1616), and the cobaltitartrate of potassium (T., 1915, **107**, 952); they were obtained as slightly alkaline emulsions by digesting the racemates or tartrates

with some excess of the alkali, and precipitating with alcohol; they contained, however, only three-quarters of the proportion of tartrate nucleus required by formula I, and were represented by the empirical formula $R_2M''M'_2,RM'',2M''O,2M'OH$. These probably represent a third stage of the action of alkalis on the tartrates, for their composition agrees with that of substances composed of a molecule of I and II together, each with an OH-group displaced by OM'. The molecule can be represented as united by means of the copper or cobalt atoms. Such a formula is in harmony with their feeble alkalinity.

The malates and lactates were examined as regards their behaviour with alkali, but definite results were obtained in the case of copper only. Here alkalinity to litmus and phenolphthalein appeared at the same time: in the case of the malate, this took place at Cu:1·03K, and in that of the lactate, at Cu:1·37K. With nickel malate, alkalinity occurred at 1·13 to 1·211K, but the point seemed to vary with the dilution. With all the other metals a precipitation occurred.

Preparation of Metallo-compound and Normal Salt.

In every case where the formation of potassium metallo-compounds was indicated by the reaction with alkali, as well as in others where no such indications were obtainable, the simple metallo-compound metameric with the normal salt has been obtained by one or other of the methods mentioned on p. 235. These may be designated for brevity sake as "by acid" or "by double decomposition."

The metallo-compound obtained by either process is an emulsion of varying degrees of solubility, although always much more soluble than the crystallised normal salt, and the latter is always deposited gradually (sometimes rapidly) from solutions of it. As seen from the following table, the lowest ratio for the solubilities of the two

Solubilities at 8°, *or where marked* *, *at* 15°.

	Tartrates.		Citrates.		Malates	
	Normal.	Metallo.	Normal.	Metallo.	Normal.	Metallo
Mn	0·072*	4·5	0·36*	∞	0·18*	∞
Fe	0·026	1·3	0·11	∞	0·37	∞
Mg	0·10*	3·0*	0·102*	2·6*	0·47*	6·3*
Zn	0·018	0·9	0·167	0·9	0·091	3·7
Cd	0·013	0·8	0·020	0·44	—	0·5*
Hg	0·002*	0·054*	—	0·007*	0·015	0·06*
Pb	0·002*	0·006*	0·003	0·012	0·012	0·14

	Racemates.	
	Normal.	Metallo.
Mn	0·018	1·23
Fe	0·045	0·9

compounds is 3:1 (lead tartrate), the ratio generally being at least 10 or 20:1.

The rapid change of the metallo-compound into the normal salt renders it impossible to obtain more than very rough values for the solubility of the former; they are generally much too low, and the entries in the table must be read as meaning merely that solutions of such a concentration have been obtained. In a few cases, even approximate values could only be obtained by precipitating the metallo-compounds, and noting the volume of water which had to be added to the mixed solutions in order to redissolve it.

In double decomposition, the bulky emulsion first precipitated may, perhaps, change directly into the compact, crystalline normal salt; but the change is generally indirect, the emulsion redissolving and the normal salt crystallising from the liquid. An explanation of this redissolution has been obtained, but cannot be dealt with in the present communication. In the cases hitherto examined, the formation of a double salt preceded or accompanied that of the normal salt (T., 1915, **107**, 948); this is not so in all those described below.

Manganese and Iron.

Tartrates. (a) *By Acid.*—The freshly-prepared carbonates were manipulated in an atmosphere of carbon dioxide. With manganese, the sole product isolated was the crystallised normal salt; with iron, a small yield of the ferrotartrate was also obtained, this drying to a nearly white, easily soluble powder.

(b) *By Double Decomposition.*—With manganese, the successive changes of the initial precipitate of metallo-compound into the double salt, and then into manganese tartrate, occur rapidly (*loc. cit.*); with iron, the latter change occupied several weeks, and is never complete at the ordinary temperature, there always being a layer of minute white needles of the double salt above the much larger, irregular yellow prisms of the single tartrate. The double salt has not been obtained pure; doubtless it is FeT,K_2T, and the product previously obtained (T., 1913, **103**, 1266), which agreed with $4FeT,Na_2T$, was a mixture. On very rapidly heating the freshly mixed reagents containing about 1 gram of iron per 100 c.c., the ferrotartrate redissolves completely, and the normal salt is precipitated at the boiling point as a well-crystallised compound of a pale straw-colour, quite free from potassium. (Found, after drying at 100°, Fe = 27·51. Calc., Fe = 27·39 per cent.). If the proportions or method of procedure are much altered, especially if the solutions are mixed while boiling, a gelatinous

or membrane-like (see p. 248) precipitate is produced which, although it cannot be washed free from potassium, is probably a modification of the single tartrate, analogous to the jellies obtained in the case of nickel tartrate, etc. (T., 1915, **107**, 953).

The normal tartrate is not easily oxidised unless it is heated when moist; treatment with certain liquids, however, which might be expected to be inert, appear to bring about oxidation: ether immediately turns it dark yellow, light petroleum does so to a somewhat less extent; chloroform, alcohol and toluene have a very slight effect of a similar character, whilst water, carbon disulphide and benzene are without action. These observations were made in view of the possible chemical action of antiseptics in the treatment of soils (*J. Agric. Sci.*, 1908, III, 35).

Racemates. (a) *By Acid.*—The yield of metallo-compound is in both cases small. The solutions of them give crystals of the normal salt in a few hours.

(b) *By Double Decomposition.*—The gelatinous precipitate of the metallo-compound rapidly becomes opaque, rendering the whole mixture semi-solid with the double salt; it liquefies in a few hours, leaving a deposit of large crystals of the impure single racemate. This may generally be obtained free from potassium by heating the mixed reagents.

To ascertain whether there existed two forms of the normal racemate, as in the case of cobalt (T., 1915, **107**, 953), crystals obtained under various conditions were examined: although differing somewhat in colour, they were found not to differ in crystalline form or behaviour; when dried at atmospheric pressure, and also at 100°, they contained, in the case of manganese, $2H_2O$ (Found, Mn = 22·66—22·97. Calc., Mn = 22·98 per cent.); at 135° they were anhydrous (Found, Mn = 27·25—27·46. Calc., 27·06 per cent.), and were not decomposed below 200°, whilst the values obtained for their solubility varied only from 0·016 to 0·019 gram of manganese in 100 c.c. at 10°. In the case of iron, the palest (of a clear, pale yellow) and darkest both contained $5H_2O$ when air-dried (Found, Fe = 19·16—18·92. Calc., Fe = 19·04 per cent.), retained H_2O at 100° (Found, Fe = 25·84—25·67. Calc., Fe = 25·23 per cent.), and became anhydrous at 150°, with slight decomposition.

Citrates. (a) *By Acid.*—The sole product is the metallo-comcompound. The emulsions are difficult to dry without liquefaction. Solutions of them yield crystals of the normal salt after some hours, and, when evaporated at 100°, they yield a residue of "scales," which, in the case of manganese, is the scale preparation sold as manganese citrate. Repeated redissolution and re-evapora-

FIG. 1.

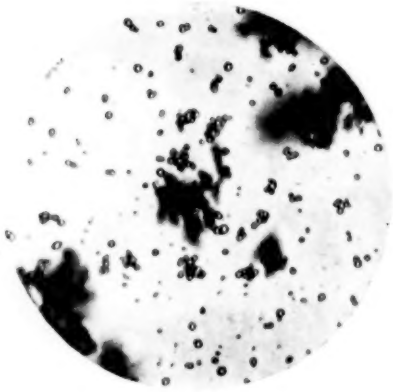


FIG. 2.

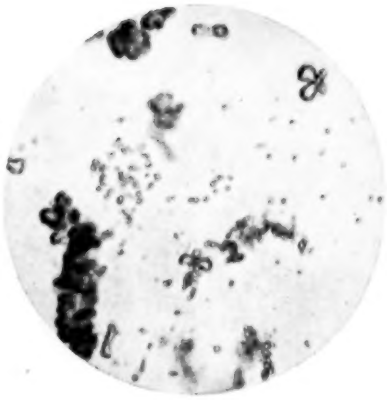
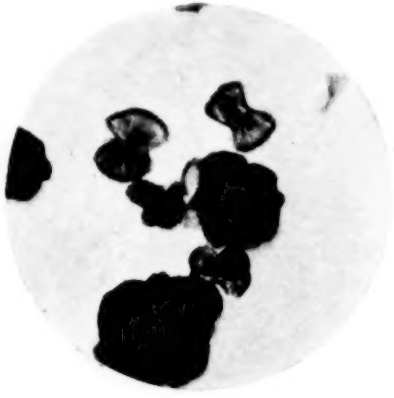


FIG. 3.



Plumbicitrate changing into lead citrate.
Magnification 200 diameters.

[*To face p.* 243.

tion converts it into the normal salt. The iron compound is not easily oxidised.

(b) *By Double Decomposition.*—With manganese, the gelatinous precipitate of the metallo-compound first formed redissolves at once, and no crystallisation occurs. With iron, there is no temporary precipitate, but minute white flakes of the normal salt eventually form: these retain $2H_2O$ at 100°.

Both manganese and iron form citrates of the type MK_4Cit_2, similar to those in other cases (T., 1915, **107**, 943). They consist of minute white crystals of great solubility, dissolving, in the case of iron, to form a dark, greenish-yellow, oxidisable solution.

Malates. (a) *By Acid.*—The metals remain entirely dissolved. The precipitated emulsions cannot be dried without the globules coalescing. Solutions of them deposit crystals of the nearly white normal salts, and on evaporation they leave residues of scales and glass.

(b) *By Double Decomposition.*—Nothing is observed until crystallisation of the normal salt begins after three or four days. Ferrous malate in solution is very oxidisable.

Lead.

Distinctive features in this case are the non-formation of a double salt, and the sparing solubility of the emulsions of the metallo-compounds.

Tartrate, Citrate and Malate. (1) *By Acids.*—The crystallised normal salt is the sole product with tartaric acid; in the other two cases the solutions, on cooling, deposit much flocculent precipitate consisting of an emulsion, and a further yield is obtainable by adding alcohol. (Plumbicitrate, after drying at 100°, contained Pb = 62·24. Calc., Pb = 62·17 per cent.) In time, or more rapidly when boiled with water, they change (indirectly, however, after first redissolving) into the nearly insoluble, crystalline, normal salts.

The change in the case of lead citrate is shown by the accompanying photographs, taken (1) at once after precipitation, (2) ten minutes, and (3) thirty minutes later. The globules redissolve, assume Brownian motion (which has interfered with the definition of 2), and the crystals simultaneously separate from the liquid. The dark patches in 1 and 2 are masses of globules which are not in focus.

(2) *By Double Decomposition.*—*Tartrate:* a mixture of prismatic crystals and globules, the latter becoming converted into crystals in a few days. *Citrate:* a mixture of globules and skin-like particles, both becoming converted into crystals in five weeks,

or more rapidly on heating. *Malate:* a very fine-grained, fairly soluble emulsion, converted into large, prismatic, sparingly soluble crystals after twenty-four hours.

Magnesium, Zinc, Cadmium, Mercury.

Most of the metallo-compounds of these metals, except mercury, are readily soluble, but, unless shaken into water in small quantities at a time, they agglomerate into a viscid mass. There is some tendency to form acid compounds where the acid process of preparation is adopted, but none to form double salts where double decomposition is employed, except in the case of mercury.

Tartrates. (1) *By Acid.*—With mercury, the main product is the normal salt in star-like clusters of crystals; in the other cases the sole primary product is the metallo-compound, which retains its solubility after drying, and from the solution of which the normal salt crystallises sooner or later. In the case of magnesium, a solution of the carbonate in the cold acid often, but not always, sets to a jelly, soluble on dilution. The mercuritartrate, when dissolved in hot water, separates as an emulsion again on cooling. Prolonged boiling decomposes it.

(2) *By Double Decomposition.*—In all cases some globules of the metallo-compound are formed, if the solutions are sufficiently concentrated; these very rapidly give place to the crystalline normal salt in the case of magnesium and zinc, and less rapidly with cadmium and mercury. With zinc, the mixed liquids, if not very concentrated, often set, after an hour, to a clear, nearly insoluble jelly, which subsequently becomes opaque, eventually leaving only a small deposit of crystals.

Citrates. (a) *By Acid.*—With zinc, some of the crystallised normal salt is produced; with the other three metals, nothing but the metallo-compound. This, in the case of mercury, separates on cooling, and also on dilution, even with hot water, without the addition of alcohol; it changes into the almost insoluble normal salt after a few days, or on continued heating, consisting then of large spheres made up of small spheres or botroidal crystals. Solutions of the other metallo-compounds yield the corresponding crystallised normal salts after a day or two, except in the case of cadmium, where the normal salt is obtained only when the solution is evaporated at the ordinary temperature; when evaporated at 100° it yields the cadmicitrate as a soluble glass, which on being moistened, breaks up into globules of emulsion. A glassy residue is likewise obtained at first in the case of magnesium and zinc, but by repeated moistening and evaporation it is converted into the corresponding normal salt. Cadmicitrate fritters at 150°. Zinci-

citrate retains $2H_2O$ at 100°, and becomes anhydrous at 130° (Found, Zn = 34·66. Calc., Zn = 34·16 per cent.), remaining quite soluble. When a solution of it is boiled, some of the emulsion separates, and redissolves on cooling. The normal salt also retains $2H_2O$ at 100°. Prolonged digestion of the carbonate with acid yields a soluble basic zincicitrate, precipitated by alcohol as an emulsion, the solution of which deposits the corresponding insoluble basic salt. The formula is $Zn_3Cit_2,Zn(OH)_2$. (Found, after drying at 170°, Zn = 38·93. Calc., Zn = 38·82 per cent.) A similar compound was obtained in the case of cobalt (T., 1915, **107**, 947). The mercury compound obtained by the acid process is a mixture of the neutral and acid salts; it contains Hg = 56·95 after drying at 100° (slight decomposition occurs at a higher temperature), Hg_3Cit_2 requiring Hg = 61·42, and HgHCit requiring Hg = 51·35 per cent.

(b) *By Double Decomposition.*—With magnesium, globules are precipitated, which soon change into hexagonal crystals; with zinc, the normal salt alone was obtained, large square crystals forming after some days; with cadmium, a stiff jelly, consisting of skin and globules, is formed, soluble on much dilution, and changing after a few hours into crystals; with mercury, the mixture gradually becomes opaque throughout several days owing to the formation of globules, after which acicular crystals appear, but some globules still remained: both contain much potassium.

Malates. (a) *By Acid.*—With mercury, some of the emulsion separates on cooling, and more when alcohol is added; it changes into botroidal crystals in a few days. With the other metals, the emulsions precipitated by alcohol are very soluble, and in the case of cadmium, no crystallisation of the normal salt from a solution of it has been obtained. A solution of cadmimalate when heated to 60°, and also when cooled to 10°, becomes cloudy through the separation of emulsion—probably not of the same composition in the two cases—which redissolves at once on cooling or heating, respectively. On evaporation, the solution of it leaves a clear glass, which on moistening becomes opaque, owing to its becoming an emulsion. Zincimalate, after being dissolved, gelatinises, the jelly eventually contracting, and becoming converted into crystals of the normal salt. Dry zincimalate changes into the normal salt in the course of some weeks.

(b) *By Double Decomposition.*—With magnesium, only the normal salt was obtained; with zinc, only zinc potassium sulphate; with cadmium, only a fine emulsion of the cadmimalate; with mercury, an emulsion, changing after some days into botroidal crystals of the normal salt.

Calcium, Strontium, Barium.

With these metals, the tendency to form acid compounds is very marked, these generally being the sole product when the carbonates are treated with acid; by using excess of the hydroxides, the neutral compounds may be obtained.

Solutions of the acid metallo-compounds tend to deposit the neutral instead of the acid normal salt. Sufficient evidence, however, has been obtained to show that both neutral and acid compounds exist in the two forms, but the change from the metallo-compound to the normal salt occurring on double decomposition, especially when the solutions are mixed gradually, is in many cases more complex than may appear from the present description, an emulsion being first precipitated, which then changes to a skin formation, and only eventually into the normal crystalline salt. An explanation of this has been obtained, but cannot be given without entering into results which must be reserved at present. There does not appear to be any tendency to form ordinary double salts with potassium as a step in the change of the metallo-compound into the normal salt, the latter being always quite free from potassium.

Glucinum has been examined, and it forms metallo-compounds, but they bear no resemblance to those of the calcium metals, and are, on the other hand, like those of ferric iron (T., 1913, **103**, 1358). A description of them will therefore be postponed until they can be compared with those obtained from other metals forming sesquioxides.

The solubilities of the compounds of the calcium metals (grams of metal in 100 c.c. at 15°) are as follows:

	Tartrates.		Citrates.				Malates.			
	Acid.		Neutral.		Acid.		Neutral.		Acid.	
	Normal.	Metallo.	Normal.	Metallo.	Normal.	Metallo.	Normal.	Metallo.	Normal.	Metallo.
Ca	0·007	—	0·018	3·2	0·11	3·9	0·07	1·4	—	—
Sr	0·04	0·36	—	—	0·016	5·2	0·004	0·4?	—	—
Ba	0·01	0·59	0·096	(0·15)*	0·023	0·55	0·44	1·21	0·14	20·0

* Much too low, owing to rapid conversion into the normal salt.

Tartrates. (a) *By Acid.*—When neutralised with the hydroxide, the normal salt alone is obtained in the case of calcium, only a very small yield of metallo-compound in that of barium, and a considerable yield in that of strontium. Solutions of these metallo-compounds deposit crystals after a time. When not neutralised, calcium gives the neutral metallo-compound, which, however, cannot be dried without becoming converted into the

corresponding insoluble normal salt. (Found, after drying at 155°, Ca = 20·83. CaT requires Ca = 21·30 per cent.) It retained $2H_2O$ at 100°. Strontium under like conditions yielded an acid compound. (Found, Sr = 28·63. SrH_2T_2 requires Sr = 28·45 per cent.) It was easily soluble, the solution becoming rapidly opaque with crystals. Barium gave a mixed product. (Found, after drying at 100°, Ba = 35·72, indicating a mixture of 75 per cent. of the neutral compound with 25 per cent. of the acid compound.)

(b) *By Double Decomposition.*—The temporary formation of globules in the case of calcium and barium, and of globules and skin in that of strontium, is observable under the microscope. These rapidly dissolve, and crystals form.

Citrates. (a) *By Acid.*—From the neutralised liquid the yield of metallo-citrate is very small in the case of calcium and barium, nil in that of strontium. The calcicitrate, but not the baricitrate, can be dried without conversion into the normal salt. When dried at 155°, the former gave Ca = 23·77; calc., Ca = 24·12 per cent.; it retained $2H_2O$ at 100°; the baricitrate gave Ba = 52·42; calc., Ba = 52·16 per cent. When not neutralised, the acid metallo-compounds, MHCit, are obtained. (*Calcium:* Found, Ca = 17·61; calc., Ca = 17·46. *Strontium:* Found, Sr = 31·94; calc., Sr = 31·56. *Barium:* Found, Ba = 41·87; calc., Ba = 41·96 per cent.) They are all anhydrous at 100°, and freely soluble after dehydration, solutions of them depositing the neutral salt unless further excess of acid is added, in which case acid salts of the type MHCit crystallise. If much excess of acid is present before the precipitation of the metallo-compound by alcohol, a hyper-acid compound, probably MH_4Cit_2, is obtained, although not in a pure state; with calcium, the compound contained 15·4 of metal, with strontium, 26·5, and with barium, 34·8 per cent., all which values are considerably lower than those required for the salts MHCit as given above.

(b) *By Double Decomposition.*—In all cases globules are first precipitated, changing rapidly into crystals free from potassium; with barium a skin formation appears as an intermediate step in the change.

Malates. (a) *By Acid.*—The neutral metallo-compounds are obtainable in all cases, but with strontium, only in small proportions, and the strontium compound is converted nearly entirely into the normal salt during desiccation at 155°. In the other cases this is not so. Where excess of acid was present, the products consisted of mixtures of the neutral and acid compounds. The barium compound gave no crystallisation from the solution after

many days, but on evaporation it left a glass mixed with crystals, and was converted entirely into crystals by repeated dissolution and evaporation.

(b) *By Double Decomposition.*—If the solutions are very concentrated, fine globules, changing into crystals, are observed under the microscope in the case of calcium; with strontium and barium, the formation of globules is not quite certain, and no crystallisation follows.

Emulsions, Jellies, and Membranes.

That the phenomena presented by the organic salts of the metals here examined are essentially the same as those presented by copper, nickel, cobalt and ferric iron, there can be no doubt. The limited solubility of some of the emulsions is, however, a novel feature in the case, and their true character would probably not have been recognised but for the microscopic examination of them; for this the author is indebted chiefly to Dr. H. B. Hutchinson. The behaviour of these emulsions, especially their separation from the liquid when it is cooled, as observed in many cases, finds a parallel in the behaviour of mixtures of phenol and water. At a sufficiently high temperature the solubilities of the two substances in each other will be infinite, and the mixture may be evaporated to dryness with nothing but insensible gradations between the liquid and solid conditions. This is what happens with those emulsions which yield a glass or scales when solutions of them are evaporated. There are cases (zincicitrate, cadmimalate) where the emulsion separates on rise of temperature, just as there are cases where the solubility of an ordinary salt diminishes with rise of temperature. According to the author's explanation of the nature of emulsions (T., 1907, **91**, 2014), the presence of solid particles surrounding the globules is necessary for the emulsion to be of a permanent character; in the case of these metallo-compounds the solid probably consists of particles of the normal salt, possibly of only molecular dimensions; these would be insoluble in the liquid already saturated with this salt. Such particles could effectively surround the globules only when these were in a liquid medium, and on the drying of this medium the particles would collect together, and the globules would coalesce; this explains the apparent melting of many of these emulsions during drying.

In many cases (the tartrates of zinc, magnesium and nickel, cadmium citrate, and the malates of nickel and zinc, as well as some of the copper salts) compounds have been obtained in the form of jellies, and in others (the tartrates of iron and strontium, lead and strontium malates, and barium and cadmium citrates)

they appear under the microscope to be made up of small irregular particles resembling those of skin or gelatin. These forms cannot be discussed fully at present, but it may be mentioned that the gelatinous and membranous conditions are probably identical, and that, whilst the comparative insolubility of most of the substances in this condition shows that they are not a form of the metallo-compound, the greater solubility in other cases shows that they are not a form of the normal salt, as was formerly suggested (T., 1915, **107**, 954).

Conclusion.

When first formed the metallo-compound appears to contain the elements of water in addition to the formula MR, but in many cases it can be dehydrated without losing its distinctive properties, and in this condition it is strictly isomeric with the normal salt, from which it differs markedly in physical properties, and in constitution; for electrolysis shows it to contain the metal in the anion. Over forty pairs of such compounds have been obtained, in which thirteen different metals and five acids figure, whilst the colour phenomena of copper salts leave no doubt that similar compounds exist in the case of all organic acids.

Whatever explanation is given of the existence of the metallo-form of copper salts must apply equally to those of the other metals now examined. That iron, manganese, cobalt, nickel, and, perhaps, lead should act as tetrads, is not surprising, but it may be thought otherwise in the case of the other metals. It is clear, however, that restricted views on the subject of valency are no longer possible. So-called saturated compounds combine with each other, and, therefore, must possess some affinity, and also valency; for valency, or definite points of attachment, is essential for combination in definite proportion. Such affinity and valency must belong to the atoms composing the molecule, for we cannot devise any system for attributing affinity and valency to a molecule if its constituent atoms possess neither. Now, the residual affinity of an atom when combined with another may be insufficient to bind to itself a third atom, but quite sufficient to satisfy the residual affinity of such an atom when it is already in a state of combination; hence residual affinity and higher valencies will come into play in the formation of complexes, although the lower valencies alone operate in the formation of simple compounds. Platinum in the compound $PtCl_6K_2$ has been shown to be united with all six atoms of chlorine, though in simpler compounds its maximum valency is 4. A similar fact has been established as regards cobalt and chromium, whilst the usually bivalent copper is quadrivalent in $CuCl_4K_2$. It is only in the case of carbon and

hydrogen, amongst the more familiar elements, that there appears to be no residual affinity and no higher valency values; and to this must be attributed the building up of compounds of these two elements in a manner which is impossible in any other case.

HARPENDEN. [*Received, October 19th*, 1915.]

XXVIII.—*Organo-derivatives of Bismuth (Supplementary Note).*

By FREDERICK CHALLENGER.

SINCE the publication of Parts I. and II. of this research (T., 1914, **105**, 2210; 1915, **107**, 16) further results have been obtained, the publication of which, in ordinary circumstances, would have been postponed. Owing to the pressure of other work, this research is temporarily suspended, but will be resumed at a later date. The recent papers of Grüttner and Wiernik (*Ber.*, 1915, **48**, 1473, 1749, 1759) also render desirable the publication of this note.

Contrary to the statement of Marquardt (*Ber.*, 1887, **20**, 1516), bismuth trichloride is readily soluble in ether, and can be employed in preparing tertiary aromatic bismuthines. *Tri*-p-*tolylbismuthine* (Michaelis and Marquardt, *Annalen*, 1889, **251**, 331) is obtained in a 60 per cent. yield from *p*-bromotoluene, magnesium and bismuth bromide in ether. *Di*-p-*tolylchlorobismuthine* (m. p. 181·5°) is obtained by mixing ethereal solutions of bismuth trichloride (1 mol.) and tri-*p*-tolylbismuthine (2 mols.). The reaction of this substance and that of the corresponding bromo-derivative with magnesium phenyl bromide has been investigated. Triphenylbismuthine (2 mols.) and bismuth bromide (1 mol.) in ether give rise to both diphenylbromobismuthine and phenyldibromobismuthine, the latter only in small quantity (compare, however, Michaelis and Marquardt, *ibid.*, 328).

This result is similar to those obtained by Grüttner and Wiernik (*ibid.*, 1749) with the corresponding stibine derivatives. When heated with sodium and toluene, phenyldibromobismuthine yields triphenylbismuthine, metallic bismuth and sodium bromide.

The instability noticed in connexion with diphenylethylbismuthine (T., 1914, **105**, 2216) seems to be characteristic of mixed aromatic aliphatic bismuthines, at least in the presence of air, since when diphenylbromobismuthine and magnesium *iso*butyl bromide interact the principal product is triphenylbismuthine.

Grüttner (*Ber.*, 1914, **47**, 3257) has prepared tri*cyclo*hexylbismuthine, and states that it is decomposed by air. This was also

observed by the author in 1913. From magnesium *cyclo*hexyl bromide and bismuth bromide in the presence of air no organo-derivative can be isolated on treating with water, bismuth oxybromide being the main product. Magnesium *iso*butyl bromide behaves similarly.

Dr. C. K. Tinkler and the author have observed that triphenylbismuthine gives colorations with certain nitro-derivatives.

Attempts to Prepare Acidic and Basic Derivatives of Quinquevalent Bismuth.

When triphenylbismuthine is dissolved in cold concentrated sulphuric acid, or when its chloroform solution is treated with chlorosulphonic acid, the phenyl groups are eliminated. The quinquevalent derivatives are much more stable under these conditions. With cold sulphuric acid, the dichloride evolves hydrogen chloride and forms a substance,* probably Ph_3BiSO_4, which reacts with ammonium hydroxide, giving a solution identical with that similarly obtained from the dichloride. With picric, tartaric or acetic acid, the solution of the dihydroxide or oxide gives crystalline salts; the acetate melts at 148—150°. The action of cold concentrated hydrochloric acid is less simple than might be expected, the dichloride not being directly regenerated.

In dilute chloroform solution, triphenylbismuthine dichloride reacts only slowly with chlorosulphonic acid, but with excess of this reagent hydrogen chloride is evolved, and yellow crystals containing bismuth, sulphur and chlorine are deposited. These decompose on heating, giving phenol and sulphur dioxide and, under other conditions, chlorobenzene.

Triphenylbismuthine and sulphuryl chloride in light petroleum give sulphur dioxide and triphenylbismuthine dichloride. Sulphur monochloride and thionyl chloride also produce the same substance, accompanied in the latter case by sulphur dioxide, organic sulphur compounds and probably diphenylchlorobismuthine.

Bismuth bromide reacts easily with a solution of the magnesium derivative of ethyl bromoacetate, giving a yellowish-white product insoluble in ether.

My thanks are due to Mr. N. A. Nicholls, B.Sc., for assistance in the early stages of this work, and to the Research Fund of the Chemical Society for a grant which has defrayed the expenses.

THE UNIVERSITY, BIRMINGHAM. [*Received, February 28th*, 1916.]

* As in the case of triphenylbismuthine dihaloids, ammonium sulphide converts this product into triphenylbismuthine.

The Recent Work on X-Rays and Crystals and its Bearing on Chemistry.

LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON FEBRUARY 3RD, 1916.

By WILLIAM HENRY BRAGG.

WHEN your Secretary asked me to speak to you to-night on the new work of *X*-Rays and Crystals, I hoped that before the time of the lecture arrived I should be able to tell you of fresh advances that had been made in the interval; but, like many other things, this research has suffered in these present times, and I have very little to tell you to-night that has not been said before. Nevertheless, I hope that I may find something that may be of interest to you, and with this aim in view I propose to consider especially those features of the new work with which chemists are most concerned.

It has been suggested to me that although this research has been described already on more than one occasion, yet it would be well for me to-night to give you an account which reaches back to the beginning. A few words of history may make a convenient opening. The origin of the work is an experiment due to von Laue, who showed that the ordered array of atoms in a crystal can behave to *X*-rays as the diffraction grating behaves to light. The actual experiments were carried out in Munich by Friedrich and Knipping at Laue's suggestion, and the author of the idea gave a fundamental description of its inner meaning in a series of papers published in Drude's *Annalen*. Laue's analysis was complicated, and it was difficult to interpret the results in a suggestive manner. The next step was made by my son, who showed that there was a simple method of interpreting the phenomenon, and from his exposition followed practically all the researches that have been carried out on this subject.

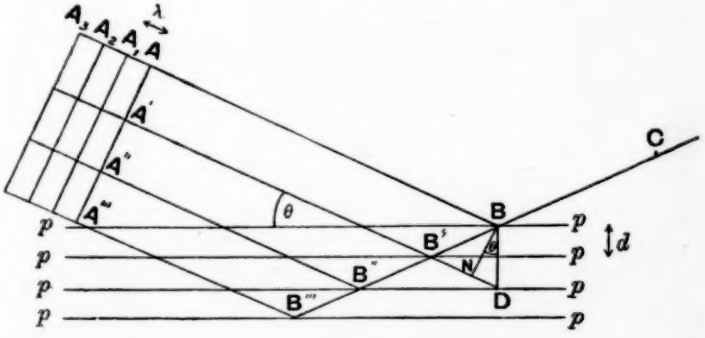
Let me now try to explain the fundamental propositions on which are based the methods that have been used. When a beam of homogeneous light falls upon a series of plane parallel surfaces, each of which reflects a small proportion of the existing light and transmits the remainder, then reflection of a very peculiar kind may take place. It is, indeed, an extension of the old phenomenon of Newton's colours on thin films.

Let the crystal structure be represented by the series of planes p, p, p; d being their common distance apart, or 'spacing.'

A, A_1, A_2, A_3 . . . are a train of advancing waves of wave-length λ. Consider those waves which, after reflection, join in moving along BC, and compare the distances which they must travel from some line, such as AA''', before they reach the point C. The routes by which they travel are ABC, $A'B'C$, $A''B''C$, and so on. Draw BN perpendicular to $A'B'$. Produce $A'B'$ to D, where D is the image of B in the plane through B'. Since $B'B=B'D$ and $A'N=AB$, the difference between $A'B'C$ and ABC is equal to ND, that is, to $2d \sin\theta$. Similarly, $A''B''C$ is greater than $A'B'C$ by the same distance, and so on.

If DN is equal to the length of the wave, or is any whole multiple of that length, all the wave trains reflected by the planes p, p, p are in the same phase and their amplitudes are added together. If DN differs but slightly from the wave-length, say

FIG. 1.



by a thousandth part, the many thousand reflections are in all sorts of phase relations with each other, and the resultant amplitude is practically zero. We see, therefore, that when a monochromatic wave train is allowed to strike the face of the crystal it is only when the glancing angle has certain values that reflection takes place. These values are given by

$$\lambda = 2d \sin\theta_1,$$
$$2\lambda = 2d \sin\theta_2,$$
$$3\lambda = 2d \sin\theta_3, \text{ etc.}$$

The reflection at the angle θ_1 is called the reflection of the first order, that at the angle θ_2 reflection of the second order, and so on.

If the crystal is slowly turned round in such a way that the glancing angle steadily increases, in general there is no reflected beam. But as the angle assumes the values θ_1, θ_2, θ_3 there is a reflection of the rays.

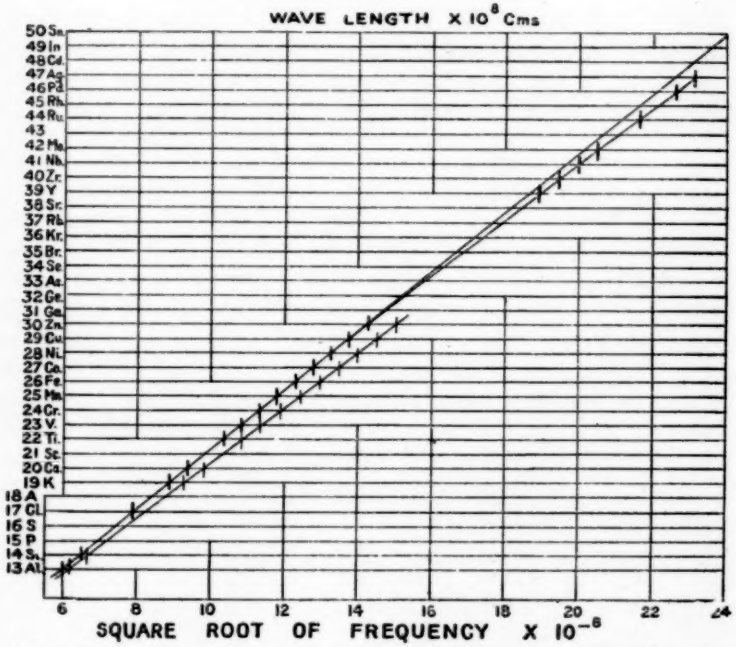
Passing to another face of the crystal which has a different spacing, d', the monochromatic rays will only be reflected when

$$\lambda = 2d' \sin \theta'_1,$$
$$2\lambda = 2d' \sin \theta'_2, \text{ etc.}$$

By comparing these results with the results of the measurements of the reflection angles of the other face we obtain the ratio of the spacings of the two sets of planes.

In a similar way, if we use always the same set of planes we

FIG. 2.



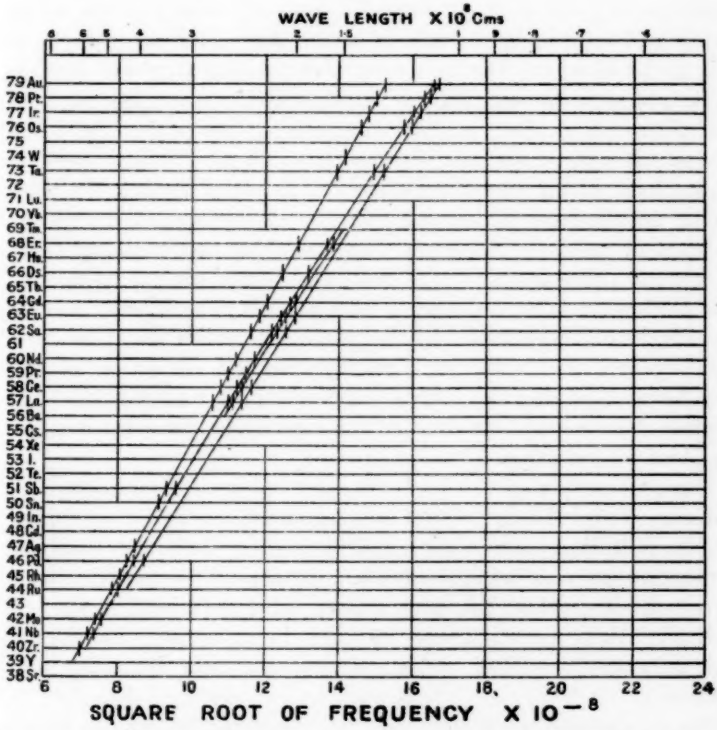
Relation of atomic number to square root of frequency of characteristic X-rays (Moseley). *K series of spectra.*

can obtain a quantitative comparison of the wave-lengths of different "monochromatic" *X*-rays.

The reflection, you see, is of a peculiar character; it does not occur unless the planes are set to the incident light at a special angle or one of a special series of angles. It is this fact on which our *X*-Ray and Crystal work is based, only we are dealing now with waves that are ten thousand times shorter than the waves of light and planes that are ten thousand times closer than the surfaces of Newton's films. Our planes are the atom-bearing planes of crystals and our waves are the waves of *X*-rays.

The length of an *X*-ray wave depends upon the metal which is bombarded in the *X*-ray bulb. Rhodium emits when so treated waves of four different lengths, the principal one having a length of 0·614 Ångström unit. Palladium in similar circumstances gives a principal wave-length of 0·583 unit; silver of 0·557. Each wave-length, you may observe, is just about 5 per cent. shorter than the one preceding.

IG. 3.



Relation of atomic number to square root of frequency of characteristic X-rays. (Moseley). *L series of spectra.*

It was the brilliant work of young Moseley, whose death in action at the Dardanelles we all so greatly deplore, which brought out this steady alteration of wave-length from atom to atom, and the diagrams of Figs. 2 and 3 are derived from his published work. Moseley showed that the *X*-ray wave-lengths obtained in this way varied more regularly from element to element than the atomic weight, and must in all probability refer to something more fundamental.

The atom-bearing planes are set in crystals at intervals of one or two Ångström units or thereabouts, and consequently wave-lengths and spacings are related to each other in about the right proportion for the occurrence of this peculiar reflection. It always seems to me a pregnant fact that this relation should exist. It might easily have been that the wave-lengths were ten or even one hundred times the atom spacings, in which case none of the work which we are considering would have been carried out.

The planes within the crystal can be imagined as drawn in many ways. We may prepare all sorts of faces parallel to such planes and measure the angle at which each such set reflects, and it is to be observed that we need not prepare the true face of a crystal, that is to say, a face parallel to the atom-bearing plane. The *X*-rays will discover for themselves the proper set of the planes. Nor need the surfaces be polished, nor, indeed, need they be prepared at all except for the convenience of setting the crystal.

Our instrument, which we call the *X*-ray spectrometer, is an instrument specially designed. It resembles the ordinary spectrometer, but there are no lenses in it, for *X*-rays cannot be refracted. The collimator is replaced by a pair of slits; the crystal stands on a central revolving table in the place ordinarily occupied by the grating, and the telescope gives way to the ionisation chamber. The latter contains the heavy gas ionised by the *X*-rays, and an electric field collects the ions of one sign and drives them into the gold-leaf electroscope.

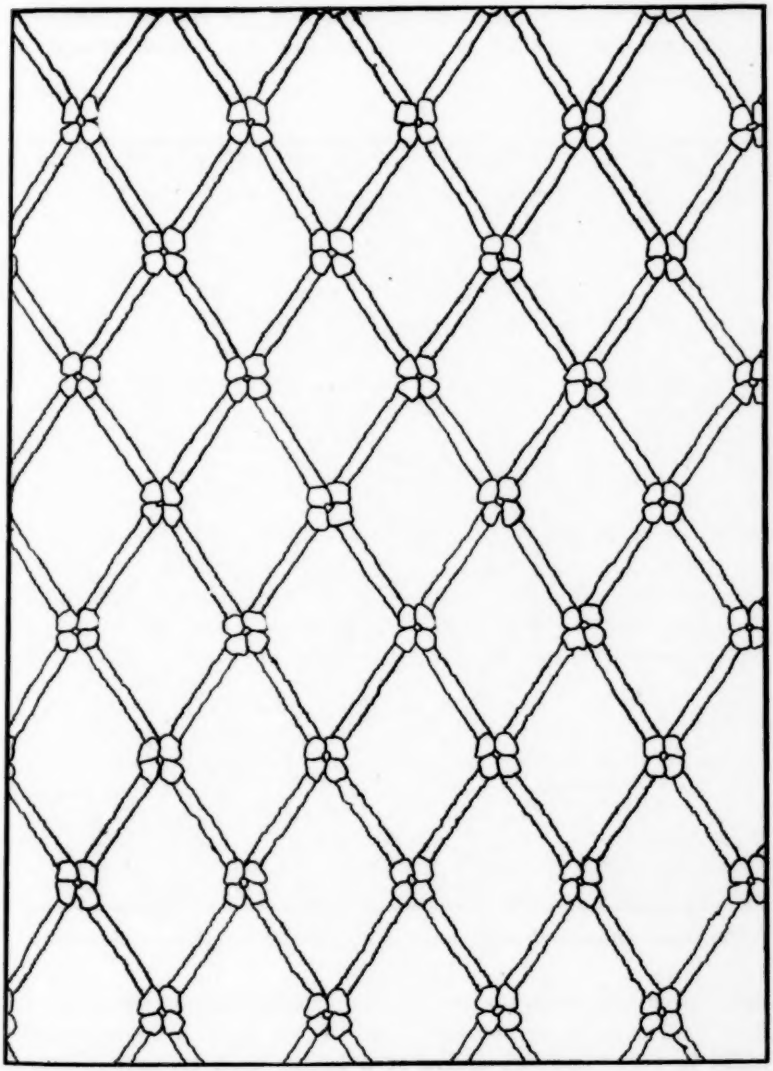
The movements of the leaf are observed by a microscope in the ordinary way. In an actual measurement we find the angles at which reflection can occur, and this can be done easily and accurately to one minute of arc. It should be noted that the *X*-ray spectrometer has one degree of pre-eminence above the ordinary light spectrometer in that it measures quantitatively, not only the angle of reflection, but also the intensity of the reflection.

Let us suppose, now, that we have measured the angles at which reflection occurs with a given wave-length and a given set of planes. We find from our formula the spacing of the set. Let us ask ourselves what it is exactly that these planes contain. To answer that question we must consider certain elementary propositions regarding the crystal structure itself.

Consider, first, a simple case in two dimensions—a wallpaper such as is illustrated in the figures. We see that a certain unit is repeated over and over again throughout the whole sheet. Let us take out some particular point in each pattern and call it the representative point. If we mark this wherever it occurs we

find we have obtained a set of points lying on what is called a lattice. In the first of the figures shown in the picture the lattice

FIG. 4

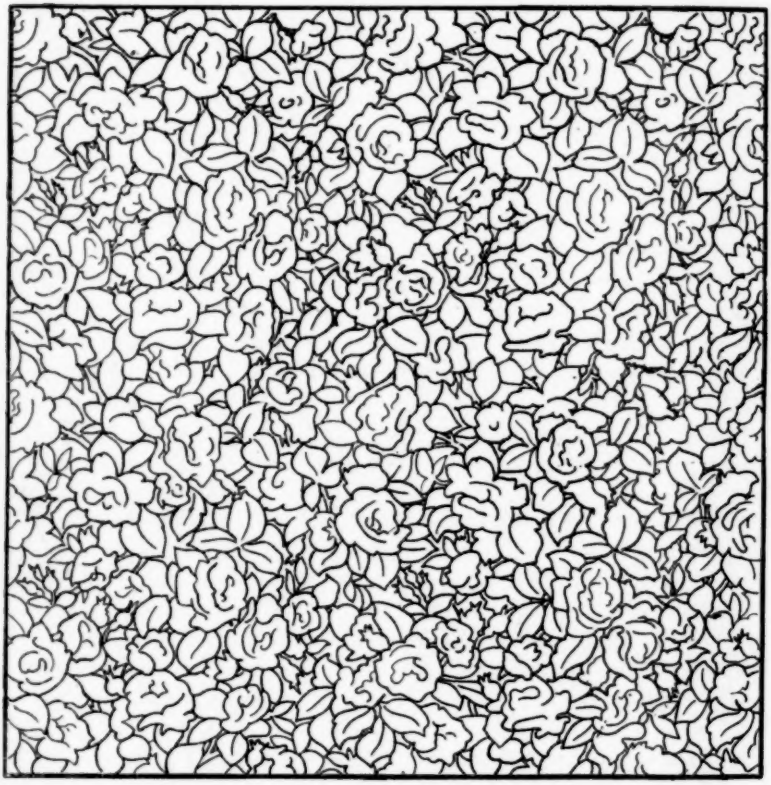


Wallpaper pattern with obvious lattice.

was obvious enough to begin with. In the second—which is specially chosen to illustrate the point I am trying to make—the

pattern is in itself very complicated. Assume that the representative point is chosen as before, and it must still lie on a lattice of a very simple pattern; however complicated the pattern of the wallpaper may be, it is based on a simple fundamental lattice. Extend this idea to three dimensions and we see that however complicated the interior of a crystal may be it must consist of

FIG. 4*a*.

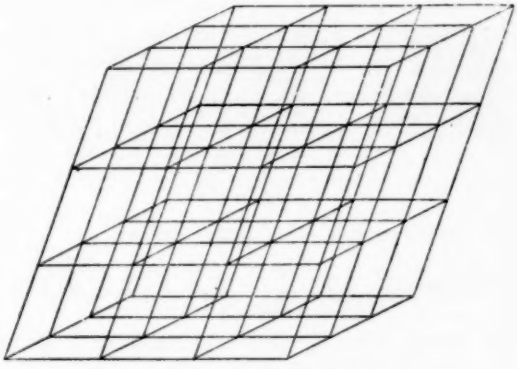


Wallpaper pattern with lattice which is not obvious, though a simple square.

units repeated in space, each unit exactly like every other in form and even in orientation; and if we mark a representative point in every unit we arrive at a lattice each element of which is a little rhomboidal cell. In its most complicated and unsymmetrical form this will still contain no more elements than three unequal sides and three unequal angles. Our method discovers the spacing of any set of planes drawn through the representative

points of the crystal. From our results we find the six unknown elements. How the atoms which constitute the unit on a pattern are arranged about their representative point is not hitherto made manifest. We shall see that this further knowledge is gained largely by the study of crystallographic symmetries and partly

FIG. 5.

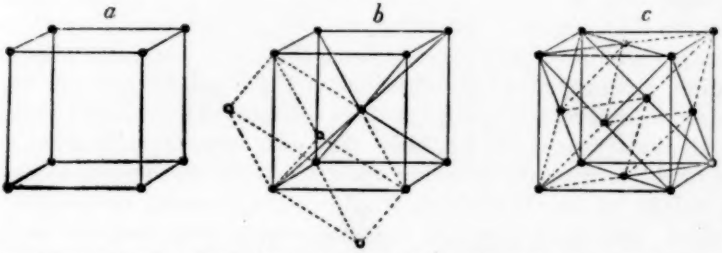


The fundamental space lattice.

also by the study of the relative intensities of the different orders in the *X*-ray spectra.

Let us begin with the crystal of simplest form—the cubic crystal. We take a cube-face of rock-salt and we find, if we assume a knowledge of the wave-length we are using, that the planes parallel to

FIG. 6.



Three forms of lattice (dotted lines in *b* and *c*) *giving cubic forms to the crystal.*

this face are spaced at intervals of 2·81 Ångström units. This does not tell us at once where our representative points lie with respect to the cube, for there are three alternative methods of arranging the points which will give cubic structure. They are shown as *A*, *B*, and *C* in the figure; the first is a simple cube,

the second a centred cube, the third a face-centred cube. It is the last of these that we find occurs most often, and perhaps there is good reason for that, because it represents the distribution with respect to each other of the centres of a system of spheres in normal piling.

The figures given (Fig. 7, *a*—*e*) show us how we may distinguish between the first and third of these alternative arrangements. An examination of these will make it clear that the spacings both of the (100) and the (110) planes of the two systems, as shown in the figures, are alike, but the (111) spacings are different, one being twice as great as the other. In fact, the relative spacings of the (100), (110), and (111) faces are in the case of the simple cube as

$$1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}},$$

whereas in the face-centred cube they are as

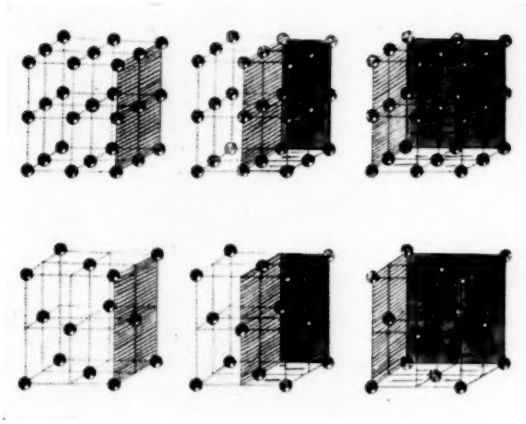
$$1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}.$$

The spectra which the faces give in each case will show these differences, as in the figures below [Fig. 8, (*a*) and (*b*)].

Now when we come to examine rock-salt we find that the spectra are not exactly like either of these two, but lie in between them [Fig. 8, (*c*)]. When, however, we replace the sodium atom by potassium, forming potassium chloride or sylvine, the spectra are such as ought to be given by the simple cube.

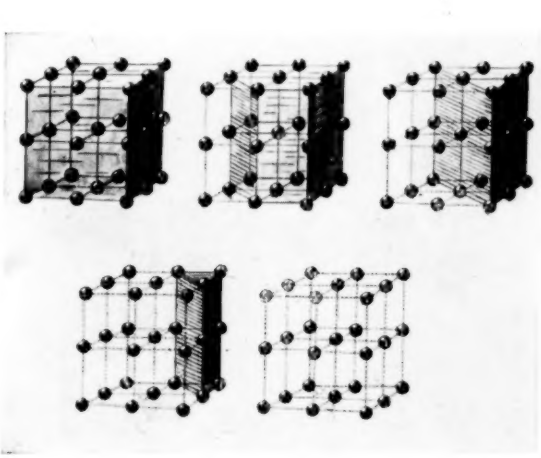
The explanation was given by my son, and will be understood from the accompanying figure (Fig. 9, p. 262), in which the full circles represent potassium and the empty circles chlorine. The arrangement is effectively equivalent to a simple cubical lattice, because the weights of potassium and chlorine are nearly equal, and X-rays therefore regard them as much the same thing; but when the sodium atom replaces the potassium, the (111) planes are now alternately of different weights. If there were no sodium atoms present at all the arrangement would be that of a face-centred lattice, and we ought to get corresponding spectra. If the sodiums were equal in weight to the chlorine we should get the spectra of the simple lattice. Being, as they are, not much more than half the weight of chlorine, the structure gives the compound spectra shown in Fig. 8 (*c*). After all, this is a fact with which we are already familiar in the case of a diffraction grating. When the lines of an ordinary grating are all alike and finely drawn, the various spectra are nearly equal in magnitude, the higher orders tending to become weaker than the lower; but if the lines are alternately strong and weak the intensities of the orders alternate also, and

FIG. 7.



(*a*).

Two arrangements, the upper a simple cubic, the lower a face centred cubic which have the same spacings for the planes parallel to a cube face (100).

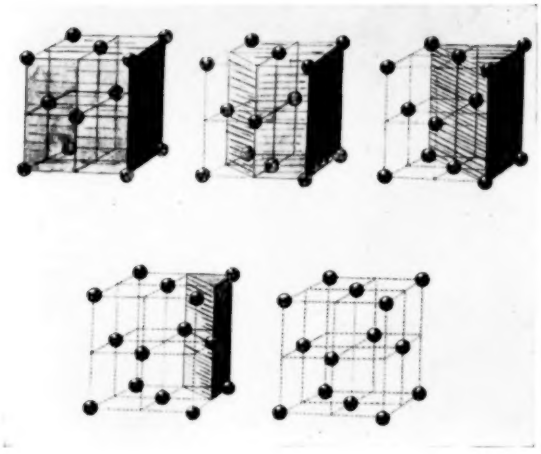


(*b*).

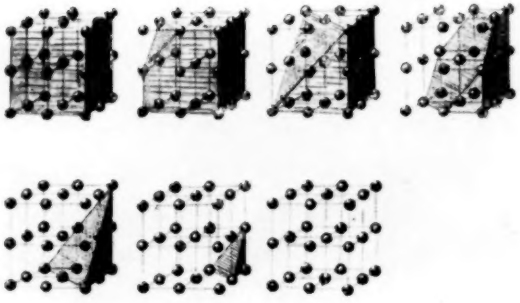
This and the next figure show that the (110) *planes also have the same spacing in the two arrangements. It is* 1/32 *of the* (100) *spacing.*

[*To face p* 260.

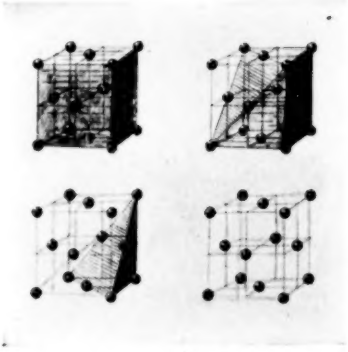
FIG. 7 (continued).



(*c*).



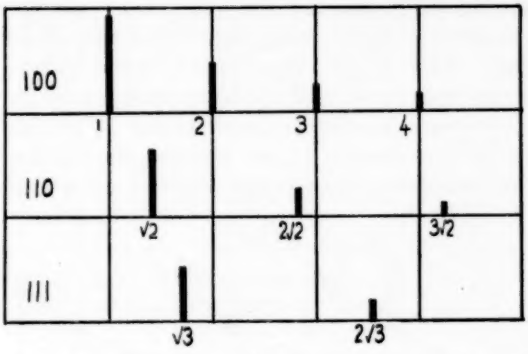
(*d*).



(*e*).

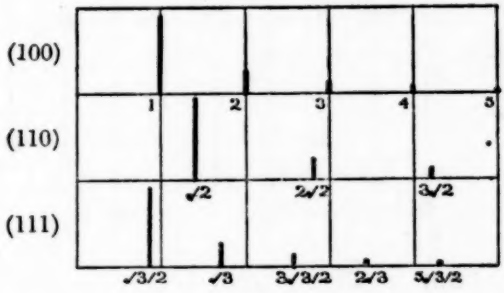
Comparison of these two figures shows that the (111) *spacing for the face centred arrangement is twice as great as for the other.*

FIG. 8.



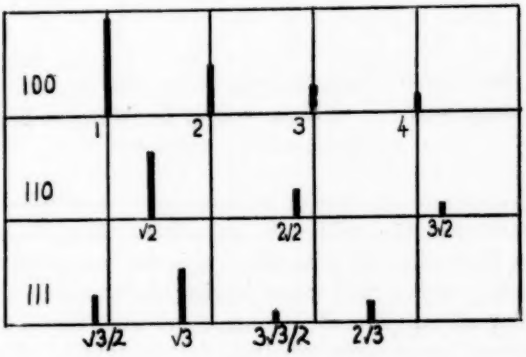
(*a*).

Diagram of spectra of simple cube.



(*b*)'

Diagram of spectra of face-centred cube.

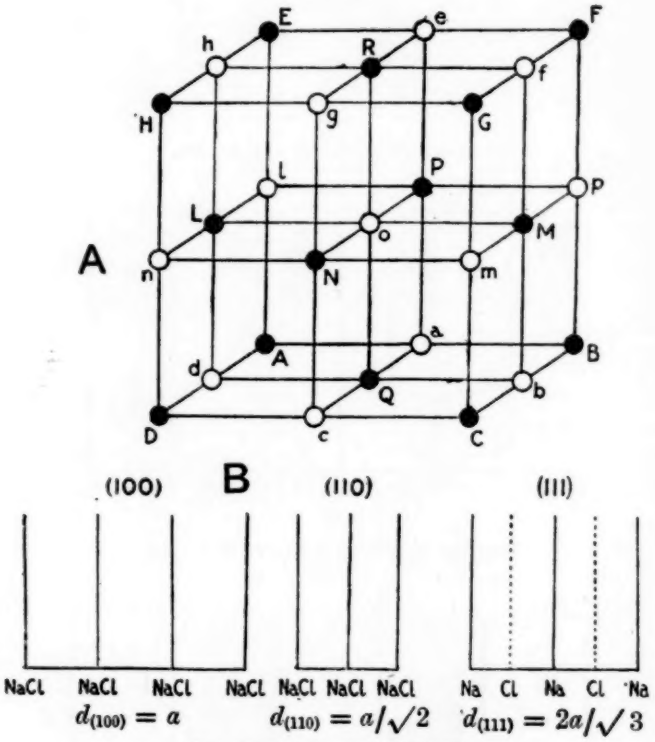


(*c*).

Diagram of rock-salt spectra.

this is exactly what we find in the (111) spectra of rock-salt. The fact is that the (111) spectra are yielded by planes which are alternately heavy and light, consisting respectively of chlorine and sodium atoms. This is the structure shown in the figure. It accounts for all the facts, and for that reason was given by my son as the structure of the rock-salt series. Certain important deductions follow at once. If we assume the structure of the figure we can calculate the spacings between atom and atom, for

FIG. 9.



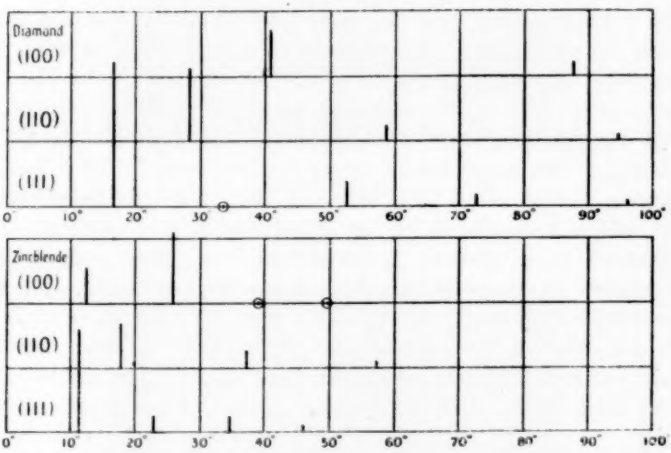
Structure of rock-salt $2a/\sqrt{3}$.

we know the specific gravity of rock-salt, we know also the weight of every atom, and the arithmetic calculation is quite easy. Thus we can say that the distance from chlorine to sodium atoms is 2·81 Ångström units, and once having determined a length of this character all subsequent measurement with the *X*-ray spectrometer becomes, not merely relative, but absolute. We can find the actual value of the spacings of any planes in any crystal, and on the other hand we can find the wave-length of any *X*-ray.

Let us consider now some results obtained with other crystals. It is curious that so many of them are based upon the face-centred lattice. In this respect, copper, silver, zinc blende, iron pyrites, fluorspar, and diamond are all alike; in every case the representative points lie on a simple face-centred lattice. It would take too long to go through the details of the determination of each of these structures. We may assume them at present, and simply examine one or two interesting consequences in certain cases.

It might be well to explain that generally we are greatly helped in the determination of the arrangement of the atoms about the representative points by two different means, the one based on a

FIG. 10.



Relative positions and intensities of spectra of diamond and zinc blende.

knowledge of crystallographic symmetries, the other based on curious differences in the intensities of the various orders of the spectra given by any one set of planes. We shall see one or two examples of this latter effect in a moment.

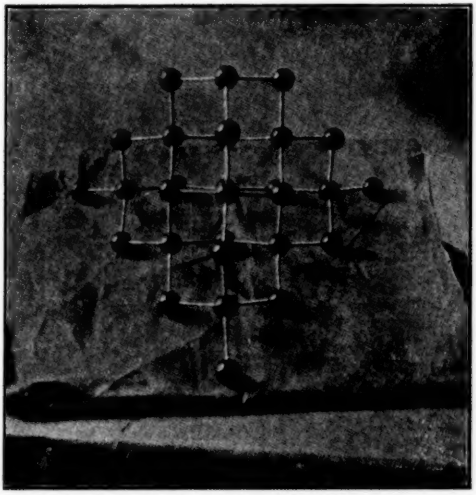
Here, for example, are the spectra of zinc blende and diamond. The spacings of zinc blende are those of the face-centred lattice, but it will be observed that in the (100) planes the odd orders are relatively weak in comparison with the even and in the (111) planes the second order is very small. The fact is that the two atoms zinc and sulphur are disposed about the representative point in a peculiar fashion, which may be thus described. Imagine a face-centred lattice of zinc atoms; imagine also a face-centred lattice of sulphur atoms, and let it proceed from coincidence with

the zinc along a diagonal of the face-centred cube to a quarter of the length of the diagonal. The odd orders of the (100) spectra are weak, because it is a feature of the structure formed in this way that the (100) planes of zinc are interleaved with planes of sulphur; and the (111) planes yield only a weak second-order spectrum, because of a peculiar arrangement in which zinc and sulphur planes alternate, with alternating spaces which are in the ratio of 1 to 3.

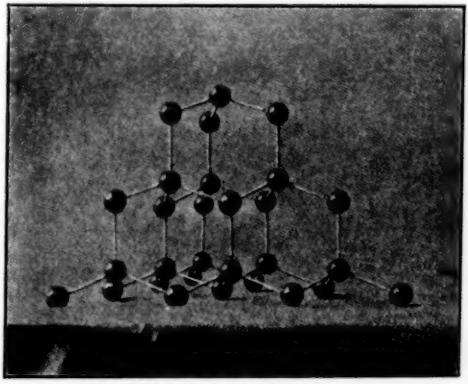
Diamond has exactly the same structure as zinc blende, there being substituted carbon atoms for both the zinc and the sulphur atoms, giving the structure shown in the figure. The spectra are like those of zinc blende, except that, on account of the equality of the two carbons, the odd orders of spectra in the (100) planes disappear entirely, and so does the second-order spectrum in the (111) planes. All this may seem a little complicated to conceive, but it appears that the structure of these crystals may be expressed in a very simple fashion. In the case of the diamond, every atom stands at the centre of gravity of a little tetrahedron formed by its four nearest neighbours, and that simple rule is sufficient for the construction of the entire crystal. It is interesting that a carbon atom thus has relations with four neighbouring atoms, which reminds us of the quadrivalency of carbon. It is also interesting to observe, as the figure shows, that carbon atoms are arranged in rings of six throughout the structure. In spite of the tetrahedral character of this structure, the diamond is not polar, because all the atoms are alike. Zinc blende, however, contains alternately zinc atoms and sulphur atoms in its (111) planes; through this and the alternation of the spacings it acquires polarity.

Calcium fluoride is of interest, because the fluorine atoms stand at the centres of all the small cubes into which the larger face-centred cubes of calcium can be divided. This gives a most symmetrical form to the crystal and explains why it stands in the highest class. Iron pyrites presents some points of special interest; the iron atoms are arranged in a face-centred lattice as before, but the sulphurs occupy peculiar positions, which can best be grasped through a study of the figures. The sulphur atoms may be supposed to have been displaced from a position corresponding with those of the fluorine atoms in the last example and to have been pushed along diagonals away from the iron atoms towards each other, but the method of choosing the directions for the movements of the various sulphur atoms is difficult to describe in words, although not difficult perhaps to understand from the figure. There is one very pretty consequence which manifests

FIG. 11.



Photograph of model of diamond. The (110) *planes are vertical and horizontal.*



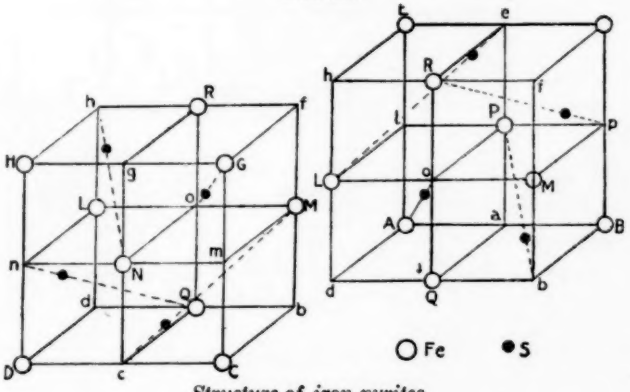
Photograph of model of diamond. The (111) *planes are horizontal*

[*To face p.* 264.

itself as soon as the structure is determined. It is well known that the iron pyrites cube has marks on its faces in the form of striations, and the lines of every face are perpendicular to the lines on the neighbouring faces. If we look through the crystal model in a direction perpendicular to a cube face, the two sulphur atoms forming a pair in each small square lie on lines which are horizontal, let us say. If the crystal is supposed to be turned round through 90°, so as to present a neighbouring face, it will be found that the pairs now lie on vertical lines. So we see that there is a difference between adjoining faces of exactly the same character as that which we know must exist in order to explain the peculiar markings of the striations of adjoining faces to each other.

The copper crystal is exceedingly simple. Native crystals can

FIG. 12.



Structure of iron pyrites.

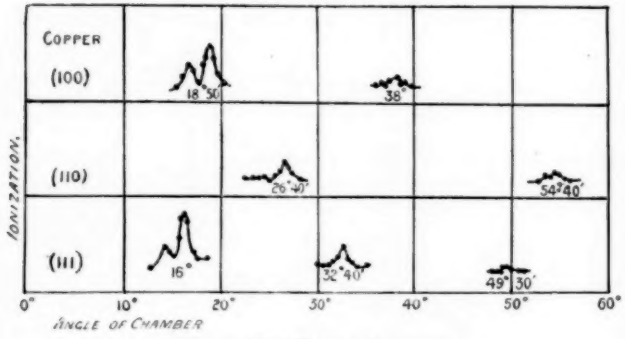
be obtained, but are not easy to work until the surface layers are etched away by acid, for these are usually so distorted as to have lost their normal arrangement. The structure is simply that of a face-centred lattice, and the copper atoms are piled on one another as shot would be.

Spinel, again, is of special interest. The model shows the construction of magnetite—one of the spinel class. It looks very complicated, yet it can be described in fairly simple terms. Imagine oxygen atoms to be piled up in simple layers, and let us fit in now the iron atoms into their proper places. Little spaces can be found between the oxygen layers, some of which are the empty spaces between four oxygen atoms; in these we find bivalent iron atoms. There are also empty spaces of another form, where three oxygen atoms of one layer lie over three of the next layer in

such a way as to fit exactly into them; but the orientations of the two sets differ by 60°. Into such spaces tervalent atoms are fitted; thus a bivalent has four oxygen neighbours and a tervalent has six.

Let me take one more instance. The structure of calcite is shown in the figure, and diagrams of consecutive (111) planes are shown also. The latter consist alternately of planes containing metal atoms only and planes containing only units consisting each of one carbon and three oxygen atoms. It is known that the calcite is symmetrical about the plane passing through the centre of one of the three faces enclosing the blunt angle of the crystal and through the edge between the other two similar faces. It might appear at first from the figure that the proper symmetry is not obtained because one side of the dividing line in the face

FIG. 13.



Spectra of Pd X-rays in copper.

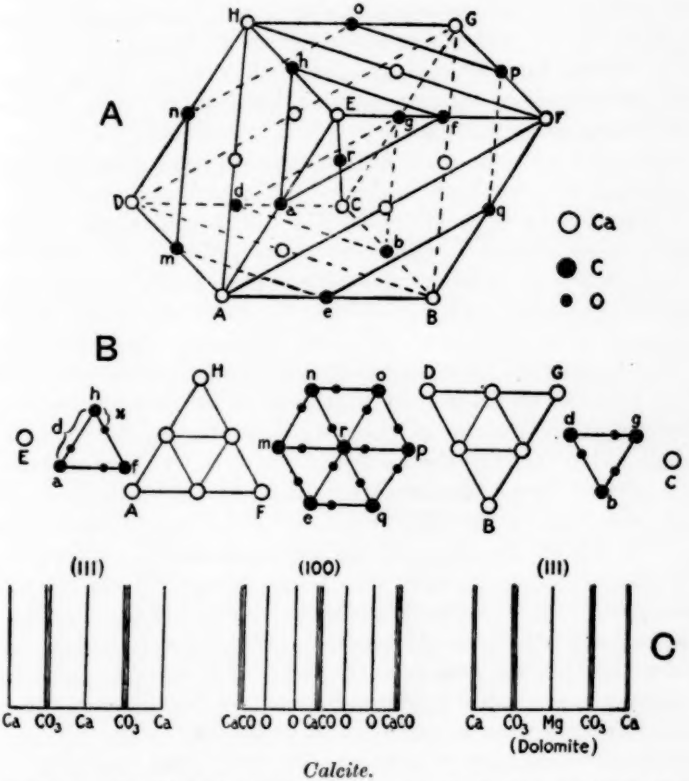
is not the mirror image of the other. It is, however, a case of *gliding* symmetry. If one side be reflected over to the other and the whole of the reflected part be allowed to glide along the other to an amount equal to the distance separating one metal atom from the next, it will be found that the fit is perfect.

Now there is a crystal called dolomite consisting of calcium magnesium carbonate. The spectrometer shows that the structure is similar to that of calcite, differing only in the fact that the layers of metal parallel to the (111) spacings are of calcium and magnesium alternately. If we now look at the (100) face of such a crystal it becomes clear that the lines of metal atoms in it are alternately of calcium and magnesium, and it will be found on trial that it is no longer possible to reflect one side of the face over the middle line and make it coincide with the arrangement on this side by allowing it to glide along. If we get the oxygen

atoms right we get the calcium where the magnesium should be, and if we get the latter right we cannot get the oxygen atoms right. Thus there is no longer any symmetry of this kind; as it is expressed by crystallographers, the symmetry of the whole crystal is degraded, and it must be put into a lower class.

Miers ("Mineralogy," p. 109) points out that the maxima of elasticity no longer lie symmetrically in the face.

FIG. 14.



Calcite.

A. Structure. B. Dissection into (111) *planes. C. Spacings of* (111) *planes.*

Such facts as these manifest themselves at the end of a determination of structure, and are to be looked upon as welcome and interesting confirmations of the accuracy of the work.

We now come to a very interesting point as to the position of the molecule in the crystal. In one sense it may be said to have disappeared, as in rock-salt, for example. The chlorine atom has six sodium atoms as neighbours, and any one of them might be

taken to be its companion in the salt molecule. As it has been put, the whole crystal is now one molecule. But that does not mean that the molecular conception is injured in any way; it only means this, that in breaking up the crystals into molecules of sodium chlorine you may begin in one of several ways. If we really take it to bits, we find that atoms pair off in molecules, although the allocation of partners is not known until we begin to pair. We are not to think of a crystal as composed of individual molecules each more or less complete in itself. On the other hand, the molecular conception is not in any way impaired; all that our work shows us is that there are alternative methods of breaking up any crystal into molecules. The surface of a crystal on this conception is more or less like an unsatisfied set of atoms to which arrangements of fresh atoms will easily be attached.

I have given a few examples of these crystal determinations; not very many have been made as yet, and there lies before us an enormous field of work. I should like to point out that the determinations that are made are quantitatively and absolutely exact in many particulars, although permitting variations of dimension in certain other particulars—variations which tend to fade away as experimental processes improve. Theories of the action of atom upon atom and molecule upon molecule must therefore be made to fit these new facts, and it would seem to be one of the important features of the work now opening before us that we shall enjoy fresh opportunities of studying molecular actions. In the crystal the atoms arrange themselves with infinite leisure, and we may take it that the positions which they finally take are those in which the simplicity of the arrangement is a very practical manifestation of the balance of mutual forces. When we think of the possibility of extending these investigations to cover all known crystals, perhaps all substances of the solid form; when we think that we are now actually and quantitatively working out the stereometry of atomic arrangements, we realise that the new powers which we possess may help us to go far.

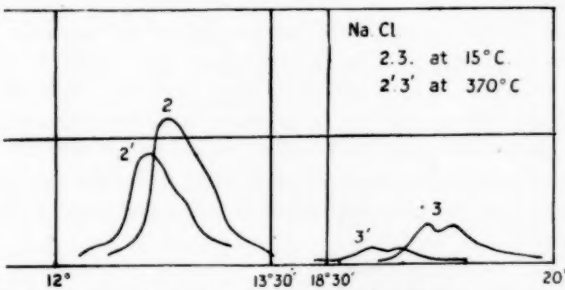
After all, the very foundation of molecular chemistry and physics is the mutual influence of atom upon atom.

I have no time to speak of all the directions in which the spectrometer is likely to aid research, but I may refer briefly to one other. We have supposed our atoms to be at rest, and there is no doubt that the facts which we observe are very much those which we should see even if the atoms were perfectly at rest. Nevertheless, we not only know that they must be in motion, but we can also make an estimate of how this motion should affect our researches. Experience confirms our anticipations. The vibration of the atoms

about normal positions ought to lead to a diminution in the intensities of spectra, particularly those of higher orders, just as the blurring of the lines of a grating leads to a parallel effect in optics. When we actually surround a crystal by a small electrical furnace and raise its temperature some hundreds of degrees centigrade, we find the intensities subsiding, particularly those of the higher orders. The figure shows also another effect which might have been anticipated through the rise of temperature: the expansion with heat draws the planes away from each other; spacings increase and the angles of reflection diminish; indeed, it is possible to determine in this way the coefficients of expansion of the crystals in different directions, and it should be remembered that the spectrometer can make use of a crystal only 2 or 3 square millimetres in area, and of very small thickness.

I must not enlarge too much upon the extent of the field that

FIG. 15.



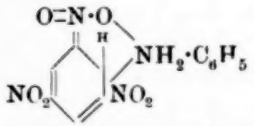
Effect of temperature on positions and intensities of second and third order spectra of (100) *rock-salt.*

lies before us. I think it will be clear that in the examination of the enormously varied forms of crystals and of the arrangement of atoms in the molecule; in the observation of the changes which occur when one atom is substituted for another; in the study of allotropic forms; in the light we may hope will be shed upon the crystalline features of metallurgy; in the power we acquire of studying quantitatively the motions of the atoms with heat; in the wholly different field of the study of *X*-rays themselves, which we must not forget although I have not considered it; in what the *X*-rays have to tell us of the nature of the atomic structure from which they come—in all this you will see there is an immense field of work before us, which may well occupy the activities of many observers for many years to come. Let us hope that the conditions may soon be such that once more we may turn ourselves with vigour and free minds to the prosecution of our researches.

XXIX.—*Additive Compounds of* s-*Trinitrobenzene with Heterocyclic Compounds Containing Nitrogen in the Ring.*

By Sosale Garalapury Sastry.

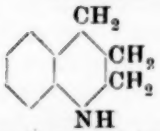
In various communications on the subject Sudborough and his co-workers have shown that various aromatic amines, phenols, phenolic ethers, and some heterocyclic compounds containing nitrogen in the ring, form additive compounds with *s*-trinitrobenzene and some other aromatic polynitro-compounds (T., 1899, **75**, 588; 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583; 1910, **97**, 773; 1911, **99**, 209; see also Hepp, *Annalen*, 1882, **215**, 344; Sommerhoff, Dissertation Zurich, 1904; Noelting and Sommerhoff, *Ber.*, 1906, **39**, 76). These compounds are relatively stable, crystalline substances, which can easily be alkylated, acetylated, and benzoylated. The influence, on the formation of the additive compounds, of introducing various alkyl, aryl, and negative groups into the ring has also been studied. The formation of the additive compound is to be provisionally attributed to the tendency of nitrogen and other multivalent atoms (as in phenols and thiophenols) to pass into a higher and saturated state of valency. Of the various formulæ that suggest themselves, the most probable one, according to Sudborough, is to be represented in conformity with the following scheme:



In the case of heterocyclic compounds and also some others, the formation of colourless or very pale-coloured compounds with *s*-trinitrobenzene seems to be in some manner due to the linking between carbon and nitrogen. The important point that was in view in the present investigation was whether in an additive compound of trinitrobenzene with an aromatic amine the presence of the linking N:C always produced a nearly complete removal of colour, as had been shown in the following pairs of compounds:

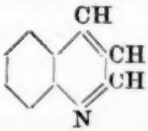
$C_6H_5\cdot CH_2\cdot NH\cdot C_6H_5$ and $C_6H_5\cdot CH{:}N\cdot C_6H_5$.

Benzylaniline. Benzylideneaniline.



Tetrahydroquinoline

and



Quinoline.

In the above pairs the substances on the left gave highly coloured additive compounds, but those on the right nearly colourless ones. In the present work this has been confirmed, the linking ·CH_2·NH· always producing compounds which are almost black.

Two other interesting additive compounds are those from phenazine and from azoxyanisole. Both have two nitrogen atoms directly linked with each other, and both the additive compounds are deep yellow.

Experimental.

*Tetrahydro-*p*-toluquinoline–*s*-trinitrobenzene,*
$C_{10}H_{13}N,C_6H_3(NO_2)_3$.

This crystallises from alcohol in brownish-black needles melting at 113°. The pure additive compound can be obtained only in the presence of excess of the base:

0·1549 gave 23·8 c.c. N_2 at 22° and 690 mm. N = 15·77.
$C_{16}H_{16}O_6N_4$ requires N = 15·56 per cent.

*Tetrahydro-*p*-toluquinoline–*s*-trinitrobenzene,*
$C_{10}H_{13}N,C_6H_3(NO_2)_3$.

This crystallises from alcohol in dark plates melting at 102°:

0·3132 gave 0·1830 $C_6H_3O_6N_3$, on being treated with dilute hydrochloric acid (compare Sudborough and Beard, T., 1910, **97**, 795). $C_6H_3O_6N_3$ = 58·43.
$C_{16}H_{16}O_6N_4$ requires $C_6H_3O_6N_3$ = 59·16 per cent.

*Tetrahydro-α-naphthaquinoline–*s*-trinitrobenzene,*
$C_{13}H_{13}N,C_6H_3(NO_2)_3$.

α-Naphthaquinoline was reduced with tin and hydrochloric acid (*Ber.*, 1891, **24**, 2475). The additive compound crystallises from alcohol in dark needles melting at 129—130°:

0·2534 gave 34·50 c.c. N_2 at 22·5° and 692 mm. N = 13·97.
$C_{19}H_{16}O_6N_4$ requires N = 14·15 per cent.

α-Naphthaquinoline–*s*-trinitrobenzene forms yellow needles melting at 133·5° (T., 1910, **97**, 773).

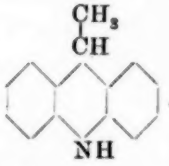
*Tetrahydro-β-naphthaquinoline–*s*-trinitrobenzene,*
$C_{13}H_{13}N,C_6H_3(NO_2)_3$.

β-Naphthaquinoline was reduced by means of tin and hydrochloric acid (*Ber.*, 1891, **24**, 2643). The additive compound crystallises from alcohol in black needles melting at 138—139°:

0·2262 gave 31·7 c.c. N_2 at 23° and 689 mm. N = 14·28.
$C_{19}H_{16}O_6N_4$ requires N = 14·15 per cent.

β-Naphthaquinoline–*s*-trinitrobenzene forms pale buff-coloured needles melting at 112° (T., 1910, **97**, 773).

5 : 10-*Dihydro*-5-*methylacridine*,



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Three grams of methylacridine (m. p. 114°) were dissolved in 150 c.c. of alcohol in a flask provided with a reflux condenser. The solution was heated to boiling, and 120 grams of sodium amalgam were added gradually through the condenser tube during about an hour and a half. The contents of the flask were kept boiling for about two hours more. After cooling, any unchanged amalgam and the mercury were separated from the alcoholic solution, which was afterwards acidified with moderately concentrated hydrochloric acid and then filtered. The residue on being crystallised from alcohol melted at 125—126°.

This dihydro-compound was converted into its *acetyl* derivative by heating it with acetic anhydride and pouring the product into water. The acetyl derivative, when crystallised from ethyl acetate, melted at 162°. On recrystallisation there was no alteration in the melting point:

0·3347 gave 21·4 c.c. N_2 at 27° and 685 mm. N = 6·30.
$C_{16}H_{15}ON$ requires N = 6·27 per cent.

5 : 10-*Dihydro*-5-*methylacridine*–s-*trinitrobenzene*,
$C_{14}H_{13}N,C_6H_3(NO_2)_3$.

This crystallises from alcohol in black needles melting at 117—118°:

0·2560 gave 33·9 c.c. N_2 at 23·5° and 688 mm. N = 13·58.
$C_{20}H_{16}O_6N_4$ requires N = 13·73 per cent.

1 : 3 : 5-*Trianilinobenzene*–s-*trinitrobenzene*,
$C_6H_3(NH{\cdot}C_6H_5)_3,C_6H_3(NO_2)_3$.

Trianilinobenzene was prepared from aniline and phloroglucinol (Minunni, *Gazzetta*, 1890, **20**, 337). The additive compound crystallises from a mixture of alcohol and ethyl acetate in black

needles and from chloroform in prisms. In either case the product melts at 160°:

0·2140 gave 31·7 c.c. N_2 at 27° and 688 mm. N = 14·91.

$C_{30}H_{24}O_6N_6$ requires N = 14·89 per cent.

Phenazine-s-trinitrobenzene, $C_{12}H_8N_2,C_6H_3(NO_2)_3$.

Phenazine was prepared from aniline and nitrobenzene by heating them together with powdered sodium hydroxide (*Ber.*, 1901, **34**, 2447). The additive compound crystallises from alcohol in yellow needles melting at 151—153°:

0·2084 gave 36·8 c.c. N_2 at 25° and 689 mm. N = 17·80.

$C_{18}H_{11}O_6N_3$ requires N = 17·82 per cent.

Azoxyanisole-s-trinitrobenzene, $C_{14}H_{14}O_3N_2,C_6H_3(NO_2)_3$.

This crystallises from alcohol in golden-yellow plates melting at 92—93°:

0·3050 gave 49·4 c.c. N_2 at 25·5° and 688 mm. N = 16·44.

$C_{20}H_{17}O_9N_5$ requires N = 16·37 per cent.

Benzylidene-1-phenyl-3-methyl-5-pyrazolone-s-trinitrobenzene.

The benzylidine derivative was prepared by heating together molecular proportions of benzaldehyde and 1-phenyl-3-methyl-5-pyrazolone, and crystallising the crude product (a red mass) from alcohol, from which it separates in red needles melting at 106—107°.

The additive compound with *s*-trinitrobenzene,

$C_{17}H_{14}ON_2,C_6H_3(NO_2)_3$,

forms scarlet plates melting at 113—114°:

0·1430 gave 22·2 c.c. N_2 at 31° and 678·5 mm. N = 14·92.

$C_{23}H_{17}O_7N_5$ requires N = 14·73 per cent.

With *s*-trinitrobenzene, dihydrophenylacridine gives a black additive compound and *s*-diphenylcarbazide gives orange needles. Tetrahydro*iso*quinoline gives only a resin.

I desire to thank Prof. J. J. Sudborough, under whose direction the present work was done, for all his kindnesses during the progress of the work.

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[*Received, February 4th*, 1916.]

XXX.—*The Periodic Evolution of Carbon Monoxide.*

By JOHN STANLEY MORGAN.

IT is generally recognised that the evolution of gases during reactions in homogeneous liquids may be considerably affected by various disturbing factors, and it is very doubtful whether the measurements of the rate of evolution of the gas can be taken as furnishing trustworthy data for the determination of the velocity of reaction.

The dehydration of formic acid by sulphuric acid is a typical reaction of the above character, and has been carefully investigated. Veley (*Phil. Trans.*, 1888, A., 257) pointed out many important features associated with it and other similar reactions. He noted a period of induction at the commencement, followed by a period of "initial acceleration." After these disturbances the reaction approached equilibrium in accordance with the law of mass, and appeared to be of the second order, although the concentration of the sulphuric acid was kept constant. These observations led him to put forward the suggestion that water was eliminated in two stages as shown below:

$$(1)\quad 2H\cdot CO_2H = \begin{matrix}H\cdot CO\\H\cdot CO\end{matrix}\!\!>\!O + H_2O$$

$$(2)\quad \begin{matrix}H\cdot CO\\H\cdot CO\end{matrix}\!\!>\!O = 2CO + H_2O.$$

At a later date and in the light of fuller knowledge he again discusses his results (*Phil. Mag.*, 1903, [vi], **8**, 271), and explains the period of initial acceleration by supposing that the gas is retained by the liquid while a supersaturated solution is being formed. Esson suggested that the rate of absorption of the gas would bear a definite relation to the rate of evolution. At the commencement it would be absorbed with greatest rapidity, and this would gradually decrease, probably in accordance with the following equation which he proposed:

$$\frac{dy}{dt} = e^{-ny}\,\frac{dx}{dt}.$$

where dy/dt represents the rate of absorption, dx/dt the rate of evolution, "n" and "y" being constants for each experiment. Veley showed that this equation satisfied his experimental results, assuming the reaction to be of the second order.

Lamplough (*Proc. Camb. Phil. Soc.*, 1908, **4**, 591) studied the reaction under conditions designed to prevent supersaturation, and found it to be of the first order.

Julius Meyer (*Zeitsch. Elektrochem.*, 1909, **15**, 506) has also investigated this change, and states it to be unimolecular.

The question has been fully discussed (*Trans. Faraday Soc.*, 1909, **5**, 1), and it is there suggested that it is unlikely that Esson's equation could take all the factors into account, since there is a possibility of such a reaction becoming highly complicated. The present author believes that some such condition has been realised, for under certain conditions the reaction is periodic in character.

Since the work in connexion with this subject was carried out, Findley and King (T., 1913, **103**, 1175) noticed that under certain conditions carbon dioxide is evolved from supersaturated solutions in a periodic manner. With this exception it is believed that all rhythmic reactions previously noted are characterised by occurring in a heterogeneous mixture, in which there is a possibility of the alternate formation and decomposition of a protective film, or in which slow diffusion effects come into play. Typical of the former type is the decomposition of hydrogen peroxide in the presence of a clean film of mercury (Bredig, *Zeitsch. physikal. Chem.*, 1903, **42**, 601). Antropoff (*ibid.*, 1908, **62**, 513) showed that a film of oxide first forms, protecting the mercury surface, and it is only on the breaking of this film that oxygen is evolved.

The second type of periodic phenomena was discovered by Liesegang, who found that when silver nitrate diffused into gelatin impregnated with potassium chromate, the resulting precipitate of silver chromate did not grow continuously, but in definite zones ("Chemische Reactionen in Gallerten," Dusseldorf, 1898). Ostwald attributed this behaviour to the formation of a supersaturated solution of silver chromate, which passes into a "labile" state on reaching a certain concentration, and is then deposited. The reaction was studied quantitatively by Morse and Pierce (*Proc. Amer. Acad.*, 1902–3, **38**, 625), whose results appear to confirm the theory.

Experimental.

After the accidental discovery of the periodic evolution of carbon monoxide, attempts were made to fix the conditions necessary, and after many failures these were determined, and it was decided to study the phenomenon by making use of Ostwald's chemograph (*Zeitsch. physikal. Chem.*, 1900, **35**, 33). The drum of the apparatus was allowed to rotate at the rate of 2·52 cm. per minute. The reaction vessel, usually a large test-tube (17·5 cm. × 3 cm.), was kept in a thermostat capable of adjustment. It was found possible to keep the temperature constant within a few tenths of a degree over long intervals of time. In some experiments the

thermometer was kept in the thermostat, whilst in others it was placed directly in the reaction vessel.

Preliminary experiments showed that the best conditions for producing the periods could be arrived at by warming about 10 c.c. of concentrated sulphuric acid to 50—60°, and then adding 1 c.c. of formic acid (D 1·2). The mixture is at once shaken, and gives a few irregular periods. After a short time it reaches a steady state, and on now adding a further small quantity of formic acid, usually 2 c.c., very pronounced periods are produced, which persist for a considerable time, gradually diminishing in intensity until they disappear, only to be again produced by the addition of more formic acid.

The appearance of the liquid while the action is in progress undergoes remarkable changes. Apparently there is no time when gas is not being evolved, for even at the minima many bubbles of gas are present, and a steady stream is evolved; this, however, increases enormously at the maxima, when a sudden creaming throughout the liquid is noticed. This is due to the instantaneous formation of innumerably small bubbles, which rapidly increase in size, rise to the surface, and there form an unstable froth, the rise and fall of which show the periodicity so plainly. The formation of this froth almost invariably accompanies the periods, and it seems to be dependent on the presence of impurities, for the purest formic acid fails to give it.

During the course of experiment it was found that the purest acid did not give periods. Fractions obtained from active acids by distillation were also different in behaviour, the higher fractions became increasingly active, and it was found that the addition of a small quantity of any of these fractions to an inactive acid was sufficient to induce periodicity.

The progress of distillation and its effect on the records obtained by means of the chemograph is shown in curves 5, 6, and 7, and the influence of the addition of a small quantity of the highest fraction to inactive acid in curves 8 and 9.

It was found more fruitful to study the effect of adding known impurities to the inactive acid rather than to attempt to isolate substances from the active acid.

It was observed during the distillation of an active acid that the fraction passing over in the neighbourhood of 107° and above was most active. Now the supposed hydrate, $H{\cdot}CO_2H,H_2O$, corresponding with the hypothetical orthoformic acid, distils at this temperature; it was therefore decided to add a small quantity of orthoformic ester to the pure inactive acid. The effect of this addition is shown in curve 13, which is decidedly periodic.

Methyl, ethyl, propyl, and amyl alcohols were tried in succession, and were found to induce periodicity of a marked character, as is shown by curves 10, 11, and 12.

Glycerol at first seemed to inhibit the periodicity, but on raising the temperature the pulsations were observed.

Gelatin caused very regular periods at 100° (see curve 14).

Dextrin caused much frothing, and gave periods marked by smaller fluctuations of pressure (see curve 15).

It was thought that if the carbon monoxide was oxidised as soon as formed to the dioxide, entirely different results would be obtained, and hydrogen peroxide did not favour the formation of periods.

Nitric acid completely changed the whole nature of the action. After the addition a momentary cessation of gaseous evolution is at first observed; a few bubbles then appear, a blue compound is produced, and almost simultaneously a violent evolution of gas, chiefly carbon dioxide and nitrogen dioxide, ensues. The liquid then clears, the blue compound once more makes its appearance, and again decomposes with great rapidity. This process is repeated several times, the blue colour finally persisting. The coloration may be discharged by the addition of porous pot or by vigorous shaking. It was found difficult to reproduce the alternate appearance and disappearance of the blue coloration, but it is always easy to form the blue compound itself. It seems possible that this blue colour is due to the formation of nitrogen trioxide, but the fact that it persists up to 100° is difficult to reconcile with this view. A very similar result is observed if nitric acid and formaldehyde are allowed to interact.

Other impurities, such as acetic and oxalic acids, formaldehyde, solid formates, and their solutions, produced no apparent effect.

The analogy between the periodic behaviour and the bumping of boiling liquids suggested the changing of the physical conditions. It was found that vigorous agitation, porous pot, increased surface relative to the volume of liquid, either entirely eliminated, or considerably reduced, the periodic evolution of gas. Temperature caused great changes; below about 40° gas was generally evolved quite regularly; above 70° the evolution becomes so violent that all rhythmic character disappears except in the presence of certain colloids.

The numerical relations between amplitudes of successive waves were determined, and also the relations between the periodic evolution and the smooth evolution of gas under similar conditions. It was found that when equilibrium had finally been attained almost the same volume of gas was evolved in both cases, and it was

assumed that the smooth evolution proceeds in accordance with the law of mass.

It will be seen from records 1, 2, 3, and 4 that by joining the maxima a smooth curve is obtained; this curve is closely related to that obtained by allowing the reaction to take place in the presence of porous pot or with agitation. The tabulated results of measurements of curves obtained at two temperatures show that there is a constant ratio between the two curves at constant temperature, and that this ratio is independent of the concentrations of the acids in the reaction mixture.

To assist in explaining the phenomena a mechanical analogy was studied. Imagine two reservoirs, *A* and *B*, so connected that water flows from one into the other, displacing air; normally this air would leave quite steadily; if, however, it is obliged to leave by means of a tube with a constricted end immersed in water, a marked periodic flow is observed. The rate of flow of the water will be influenced but little by the periodic escape of the air, but will depend on the head of water which is maintained. Water will continue to flow from *A* into *B* until sufficient pressure has been accumulated to overcome the forces of friction and capillarity at the nozzle; as soon as this point is reached a sudden rush of air takes place, and one might obtain a measure of the accumulated pressure in *B* by making use of a recording device. As soon as the pressure has been released the jet is again sealed by the water until another accumulation of pressure serves to force an outlet; this action is repeated at gradually increasing intervals, smaller and smaller quantities of gas being delivered at each outflow.

This analogy, whilst not perfect, is sufficient to help in the explanation of the problem. The pressure attained at the commencement of a period is a function of the time, and is simply related to the pressure which would have been attained had a smooth evolution of gas taken place. It is readily seen that the result of imposing a periodic flow has, in the physical analogy, been equivalent to moving the curve representing the smooth flow in a direction at right angles to the ordinate, and thus obtaining a curve steeper at any point, but related to the smooth curve by a constant ratio. This is, therefore, similar to the case under consideration.

It is thought that the evidence accumulated with respect to the periodic evolution of carbon monoxide shows that it is a supersaturation phenomenon, and the following explanation is advanced. It is assumed that the actual decomposition of the formic acid proceeds smoothly, but the evolution of the gas is retarded until the solution thus produced attains such a concentration that spontaneous evolution ensues in accordance with Ostwald's theory

("Lehrbuch," II, ii, 780). Suppose it is necessary, in order to produce this result, that equal volumes of gas are evolved. As soon as the requisite quantity of gas has been formed it will be liberated with a violent rush, and will be followed up by a further quantity of gas, which takes the opportunity of escaping at the pressure that would be normal if the reaction were proceeding smoothly. If this is repeated, the course of evolution will be as follows. The first evolution of gas will take place at a pressure higher than any attained normally; the rate at which the flow ceases will not be so rapid as its commencement; the periods of non-evolution will gradually increase in length, depending on very complicated factors; the heights attained by the maxima on the records will become smaller and smaller, but will probably bear a constant ratio to the height of the corresponding smooth curve.

Reference to the records will show how far the facts are explained by the above simple hypothesis. It is suggested that the influence on the limits of supersaturation attained and on the quantity of gas liberated over and above that which has been absorbed may be influenced very considerably by small quantities of impurities.

Whilst the above explanation seems adequate for the simple cases, it may be that the case of nitric acid is entirely chemical. Lotka (*J. physical Chem.*, 1910, **14**, 271) has shown how it is possible for the resultant of several reactions which co-exist to assume a periodic character in a homogeneous mixture. It is necessary that there should be three reactions, one of which gives rise to an autocatalytic decomposition product. If it can be shown that the blue compound which is produced in the presence of nitric acid is an autocatalytic decomposition product, the conditions would be very suggestive of those assumed by Lotka.

If the supersaturation theory is correct, it is thought that periodic phenomena may occur much more frequently than is supposed. The following cases have been observed in support of this view. Calcium carbonate was dissolved in acetic acid; the gas commenced to escape in a very pronounced rhythmic manner. Supersaturated solutions of sodium thiosulphate and potash alum have have been observed to crystallise in perfect waves by using very thin films. The similarity of these waves to the various types of cloud showing a waved form suggests that these may be the result of supersaturated vapour meeting a cold zone in an atmosphere free from nuclei.

Later work will, it is hoped, establish the conditions necessary to produce these and other periodic phenomena more exactly, and show to what extent they are chemical or physical in character.

Temperature 52·8°.

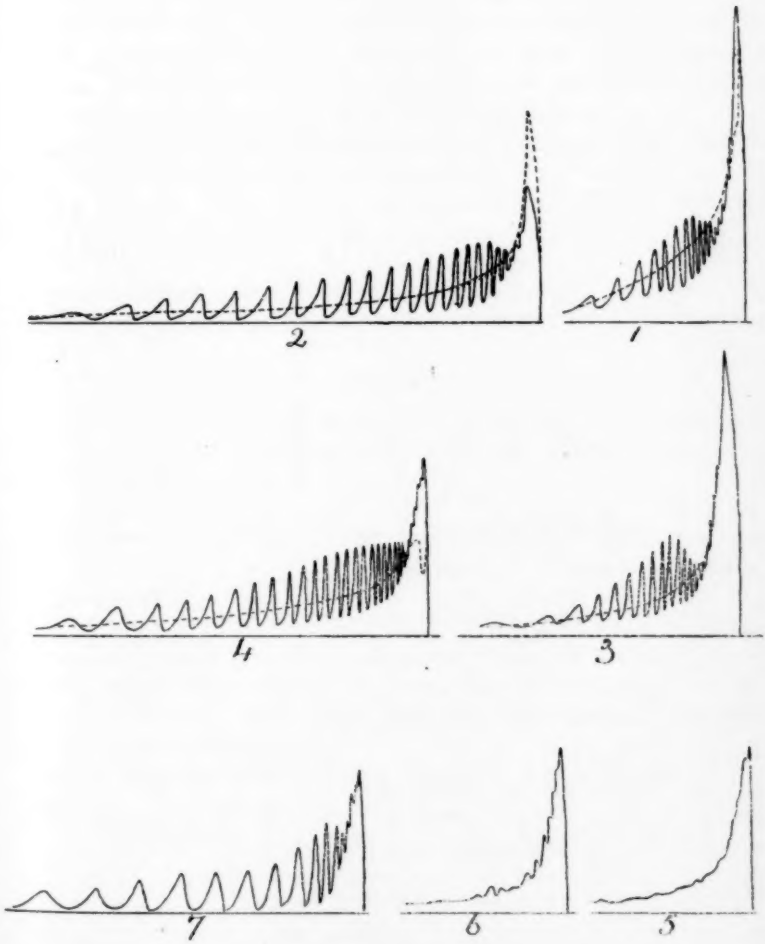
	Altitude of periods.	Corrected *P*.	Corresponding altitude of smooth curve.	Corrected *S*.	Ratio *P*/*S*.
1*a*	1·90	3·6	1·2	2·2	1·7
	1·75	3·4	1·1	2·0	1·7
	1·57	2·9	0·9	1·8	1·6
	1·30	2·4	0·75	1·6	1·5
	1·12	2·1	0·6	1·3	1·6
	0·91	1·8	0·5	1·1	1·6
	0·60	1·35	0·32	0·9	1·5
1*b*	1·65	3·2	1·11	2·1	1·5
	1·60	3·0	1·0	1·94	1·6
	1·57	2·9	0·94	1·9	1·5
	1·53	2·8	0·85	1·75	1·5
	1·43	2·7	0·8	1·65	1·6
	1·40	2·65	0·75	1·6	1·6
	1·36	2·5	0·68	1·53	1·7
	1·25	2·4	0·64	1·40	1·7
	1·21	2·3	0·61	1·37	1·5
	1·10	2·1	0·58	1·3	1·5
	0·93	1·9	0·52	1·2	1·6
	0·85	1·75	0·48	1·13	1·5
2*b*	1·60	3·0	0·77	1·63	1·8
	1·45	2·7	0·70	1·5	1·8
	1·30	2·4	0·64	1·4	1·7
	1·21	2·3	0·61	1·37	1·7
	1·09	2·0	0·55	1·25	1·7
	1·00	1·95	0·51	1·2	1·6
	0·95	1·9	0·46	1·07	1·8
	0·90	1·8	0·42	1·05	1·7
	0·85	1·75	0·38	0·98	1·8
	0·80	1·65	0·34	0·95	1·7
	0·76	1·61	0·31	0·9	1·6
	0·72	1·55	0·29	0·84	1·8
	0·66	1·4	0·27	0·81	1·7
	0·60	1·35	0·25	0·79	1·7
				Mean Ratio	1·63

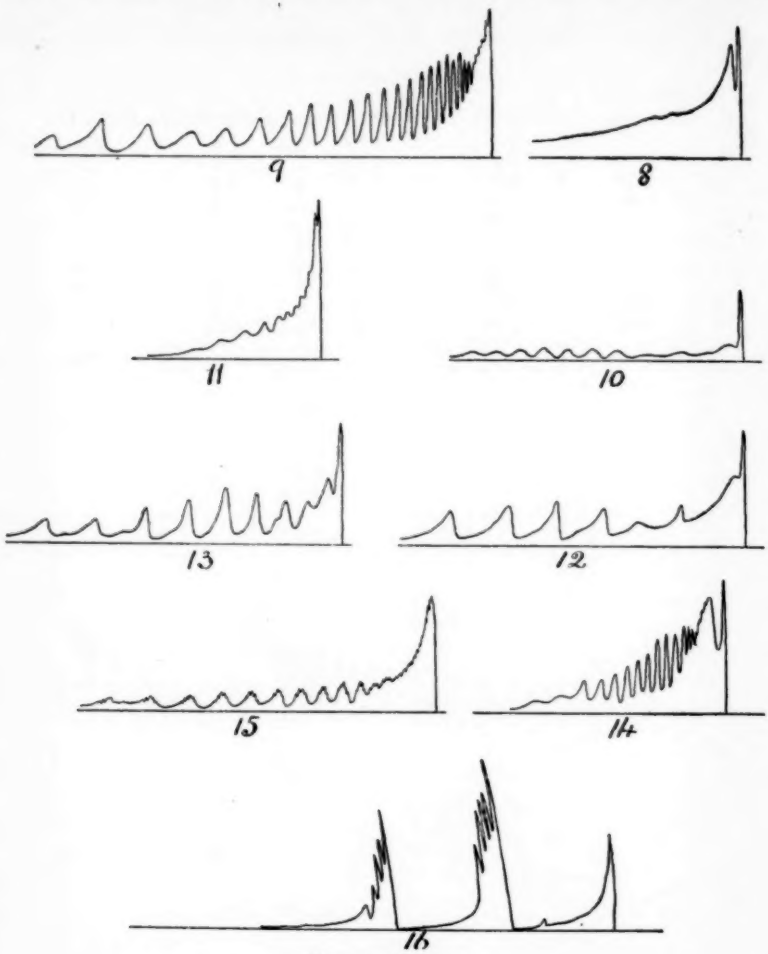
Temperature 61·5°.

3*a*	2·50	4·8	0·95	1·9	2·5
	1·93	3·6	0·82	1·7	2·1
	1·73	3·4	0·76	1·6	2·1
	1·52	2·7	0·68	1·45	1·9
	1·33	2·5	0·61	1·37	1·8
	1·14	2·2	0·46	1·07	2·0
	1·00	1·95	0·38	0·98	2·0
	0·77	1·62	0·27	0·81	2·0
3*b*	1·35	2·71	0·61	1·37	2·0
	1·30	2·40	0·53	1·20	2·0
	1·19	2·25	0·50	1·16	1·9
	1·11	2·10	0·48	1·13	1·9
	1·08	2·00	0·44	1·00	2·0
	1·05	1·98	0·40	0·98	2·0
	1·00	1·95	0·34	0·95	2·0
	0·94	1·90	0·32	0·9	2·1
	0·89	1·77	0·30	0·85	2·1
	0·85	1·75	0·27	0·81	2·1
	0·80	1·65	0·26	0·80	2·1

Temperature 61·5° (*continued*).

	Altitude of periods.	Corrected *P*.	Corresponding altitude of smooth curve.	Corrected *S*.	Ratio *P*/*S*.
4*b*	1·77	3·5	0·65	1·4	2·5
	1·65	3·2	0·62	1·37	2·3
	1·56	2·9	0·57	1·3	2·2
	1·50	2·8	0·55	1·25	2·2
	1·39	2·65	0·52	1·22	2·1
	1·25	2·4	0·49	1·14	2·1
	1·15	2·2	0·46	1·1	2·0
	1·07	1·98	0·42	1·05	1·9
	0·95	1·9	0·32	0·88	2·1
	0·87	1·77	0·30	0·86	2·0
				Mean Ratio	2·04





Key to Curves.

1. Curves obtained by 2nd addition of 2 c.c. formic acid at 52·8°
2. „ „ „ 3rd „ „ 2 c.c. „ „ „ 52·8°
3. „ „ „ 2nd „ „ 2 c.c. „ „ „ 61·5°
4. „ „ „ 3rd „ „ 2 c.c. „ „ „ 61·5°

Dotted curve obtained by taking similar mixtures but with vigorous shaking.

5. Curve obtained from fraction boiling at 100–105°.
6. „ „ „ „ „ „ 105–107°.
7. „ „ „ „ „ „ 107–109°.
8. „ „ with pure formic acid.
9. „ „ with pure formic acid with addition of 0·1 c.c. of residue 109°.
10. „ „ with addition of ethyl alcohol.
11. „ „ „ „ „ propyl alcohol.
12. „ „ „ „ „ amyl alcohol.
13. „ „ „ „ „ formic ester.
14. „ „ „ „ „ gelatin at 100°.
15. „ „ „ „ „ dextrin.
16. „ „ „ „ „ nitric acid (rate of drum doubled).

In conclusion, the author wishes to thank Professor Lapworth for the interest he has shown in the work, and for many helpful suggestions made by him.

MANCHESTER UNIVERSITY. [*Received November 2nd*, 1915].

XXXI.—*Chloro- and Bromo-triethylphosphinoacetaldehyde.*

By WILLIAM CALDWELL.

HOFMANN (*Proc. Roy. Soc.*, 1860, **10**, 614) studied the action of triethylphosphine on ethylene bromide, and obtained several additive products, one of which had the formula $CH_2Br{\cdot}CH_2{\cdot}PEt_3Br$, which on treatment with silver hydroxide gave the analogue of choline, namely, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_3{\cdot}OH$, and on further boiling with silver hydroxide gave $CH_2{:}CH{\cdot}PEt_3{\cdot}OH$.

The above-mentioned dibromo-additive compound when acted on by silver acetate and the filtrate evaporated with hydrochloric acid gave a chloride which, when precipitated with platinic chloride, yielded the platinum salt of a compound, $CH_2{:}CH{\cdot}PEt_3{\cdot}OH$, analogous to neurine.

Hofmann also found that some of the vinyl compound was formed in the interaction of triethylphosphine and ethylene dibromide, thus:

$$C_2H_4Br_2 + 2Et_3P = CH_2{:}CH{\cdot}PEt_3Br + Et_3PHBr.$$

Later, by the action of triethylphosphine on monochloroacetic acid, Hofmann (*Proc. Roy. Soc.*, 1861, **11**, 530) obtained an ethylated phosphorus betaine.

In connexion with these researches, it is interesting historically to note that the study of the phosphorus derivatives preceded that of the analogous nitrogen compounds. Strecker discovered choline in 1862, whilst Liebreich obtained neurine in 1865, and later obtained the base oxyneurine by the action of monochloroacetic acid on trimethylamine; Scheibler (*Ber.*, 1869, **2**, 292; 1870, **3**, 155) subsequently showed that this was identical with a basic substance occurring in the sugar-beet (*Beta vulgaris*), to which he gave the name betaine.

The relationships between these substances are as follows:

Nitrogen derivatives:

$OH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$ Choline. $\qquad$ $CH_2{:}CH{\cdot}NMe_3{\cdot}OH$ Neurine.

$CO_2H{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$.
Betaine.

Phosphorus derivatives:

$$OH\cdot CH_2\cdot CH_2\cdot PEt_3\cdot OH \qquad CH_2{:}CH\cdot PEt_3\cdot OH$$
$$CO_2H\cdot CH_2\cdot PEt_3\cdot OH.$$

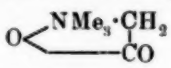
Choline and betaine are related to each other as alcohol to acid, and the intermediate or aldehydic compound, $CHO\cdot CH_2\cdot NMe_3\cdot OH$, has also been synthetically obtained by Berlinerblau (*Ber.*, 1884, **17**, 1140) from the interaction of monochloroacetal and trimethylamine and by treating the additive product, $OEt_2\cdot CH\cdot CH_2\cdot NMe_3Cl$, with barium hydroxide.

Meanwhile Schmiedeberg and Koppe (Leipzig, 1869) had isolated a substance from fly agaric which they named "muscarine," having the empirical formula $C_5H_{15}O_3N$; this, like neurine, can yield trimethylamine on destructive distillation, and possesses a powerful physiological action. In Berlinerblau's paper (*loc. cit.*) the following relationships are given:

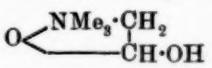
$$OH\cdot CH_2\cdot CH_2\cdot NMe_3\cdot OH \qquad CH(OH)_2\cdot CH_2\cdot NMe_3\cdot OH$$
Choline. Muscarine.

$$CO_2H\cdot CH_2\cdot NMe_3\cdot OH.$$
Betaine.

Subsequently Emil Fischer (*Ber.*, 1893, **26**, 468), by methylating aminoacetal with methyl iodide, obtained the compound $CH(OEt)_2\cdot CH_2\cdot NMe_3I$, analogous to Berlinerblau's additive product of monochloroacetal and trimethylamine; by boiling the corresponding chloride with hydrochloric acid it was hydrolysed, with the production of betainealdehyde, and was apparently identical with Berlinerblau's compound. He gave the following formulæ:



Betaine.



Betainealdehyde.

Whether betainealdehyde is identical with muscarine appears to be very doubtful, and in fact the evidence appears to point in the other direction, Nothnagel (*Ber.*, 1893, **26**, 801) finding marked differences in physiological action, and it is possible that the difference is one of hydration, and muscarine may stand to betainealdehyde as chloral hydrate does to chloral, and consequently may be represented by Berlinerblau's formula already given.

The object of this investigation, therefore, was to prepare a phosphorus aldehyde derivative intermediate between the phosphorus derivative analogous to choline and the phosphorus derivative analogous to betaine by repeating Berlinerblau's and Fischer's experiments, substituting triethylphosphine for trimethylamine.

Experimental.

Interaction of Triethylphosphine and Monochloroacetal.

The monochloroacetal used in the experiments was prepared with slight modifications according to the method adopted by Berlinerblau (*Ber.*, 1884, **17**, 1140). It was purified by fractional distillation, the portion boiling between 156° and 158° being alone used.

Equivalent proportions of monochloroacetal and triethylphosphine were sealed in a tube, and after being kept overnight a small quantity of a white, crystalline product separated. The contents of the tube were heated at 100° for some hours and a syrupy liquid separated in quantity, but in order to complete the reaction it was found necessary to heat the mixture at 115—120°. The product was a viscous liquid readily soluble in water, and on treatment of the aqueous solution with platinic chloride a sparingly soluble, yellow, crystalline salt was obtained which, when recrystallised from alcohol, separated in long, yellow needles:

0·4271 * gave 0·0948 Pt and 0·418 AgCl. Pt = 22·19; C = 24·15.

$(C_{12}H_{25}O_2ClP)_2PtCl_4$ requires Pt = 22·2; Cl = 24·23 per cent.

It may be mentioned that much difficulty was experienced in estimating the platinum in these phosphorus platinum salts. On several occasions three to four days' continual treatment with hydrogen sulphide with simultaneous heating was necessary completely to precipitate the platinum, and in one or two cases even that treatment failed—traces of platinum remaining in solution. This method of analysis had finally to be abandoned, and the platinum was precipitated as metallic platinum by means of an alkaline formate. In this case, too, some difficulty was experienced: the finely divided precipitate constantly passed through the filter, but eventually that difficulty was overcome by keeping the wash-water alkaline by the addition of ammonia. The results obtained by this method were very satisfactory as regards both platinum and chlorine.

Wallach's method (*Ber.*, 1881, **14**, 753) of precipitation with sodium ethoxide was not found so satisfactory.

A salt obtained with gold chloride from the ether of chlorotriethylphosphinoacetaldehyde could only be obtained as an oil, and since it showed a tendency to crystallise it was not further examined.

* Dried over sulphuric acid.

Interaction of Triethylphosphine and Monobromoacetal: The Ether of Bromotriethylphosphinoacetaldehyde.

Monobromoacetal was prepared by adding bromine drop by drop to acetal mixed with calcium carbonate (*Ber.*, 1892, **25**, 2551). The resulting liquid was washed with sodium hydroxide, followed by water, dried, and then fractionated. The portion boiling between 164° and 172° was used. The monobromoacetal reacted with triethylphosphine at the ordinary temperature, and gave a colourless liquid.

Chlorotriethylphosphinoacetaldehyde.

The additive product obtained by the action of triethylphosphine on monochloroacetal after washing with ether to remove unchanged triethylphosphine was dissolved in six times its weight of concentrated hydrochloric acid and heated at 100° in an open dish until the solution became of a syrupy consistency. The product after remaining for several days in a vacuum over solid sodium hydroxide, yielded a crystalline product, which was squeezed in a linen bag to free it from mother liquor, and then dried on a porous tile in the desiccator over sulphuric acid. The crystals were found to be excessively readily soluble in water, ethyl and amyl alcohols, or ether. From boiling chloroform, in which it is less readily soluble than in any of the above solvents, it crystallised after some time in leaflets clustering into stellate masses. The crystals after some days passed into solution again.

The identity of the new compound was established by a determination of chlorine (by Volhard's method) in the product obtained as just described, and dried on a porous tile in a vacuum over solid sodium hydroxide, and also by an analysis of the platinichloride:

0·2428 required 12·28 c.cm. $N/10$-$AgNO_3$ (Volhard's method). Cl = 18·09.

$C_8H_{18}OClP$ requires Cl = 18·05 per cent.

The compound was dissolved in water, and on the addition of platinic chloride an orange-yellow salt was obtained in minute octahedra. The *platinichloride* was dried over sulphuric acid in a vacuum until the weight remained constant:

0·3276 gave 0·3135 CO_2 and 0·1575 H_2O. C = 26·1; H = 5·31.
0·7684 „ 0·2064 Pt and 0·8894 AgCl. Pt = 26·8; Cl = 29·0.
$(C_8H_{18}OClP)_2PtCl_4$ requires C = 26·31; H = 4·93; Pt = 26·7; Cl = 29·1 per cent.

Properties of Chlorotriethylphosphinoacetaldehyde.

In the following properties the aldehydic character of the new compound is clearly seen:

(1) An ammoniacal solution of silver hydroxide was reduced with the formation of a mirror.

(2) A little diazobenzenesulphonic acid was suspended in water and a few drops of sodium hydroxide solution were added. On the addition of a trace of chlorotriethylphosphinoacetaldehyde followed by a fragment of sodium amalgam, a reddish-violet colour was obtained.

The platinichloride exhibited the same reducing properties.

Interaction of Triethylphosphine and Bromoacetaldehyde: Bromotriethylphosphinoacetaldehyde.

Bromoacetaldehyde was prepared by heating bromoacetal with anhydrous oxalic acid (*Ber.*, 1892, **25**, 2552), and equivalent proportions of this substance and triethylphosphine were sealed in a tube. The reaction began at the ordinary temperature with a deposit of a white, crystalline compound. At 100° in the water-bath the reaction was completed in eight hours. The product was washed with dry ether, transferred to a porous tile, and finally dried over sulphuric acid in a vacuum until the weight remained constant.

Bromotriethylphosphinoacetaldehyde is a deliquescent substance, but it may be precipitated in the crystalline form from an alcoholic solution by the addition of ether. Long, rectangular, parallelopiped-shaped, crystalline needles are likewise obtained from the alcoholic solution of the substance after keeping for some time:

0·1389 gave 0·2027 CO_2 and 0·1063 H_2O. C = 39·8; H = 7·78.

0·824 „ 0·6469 AgBr. Br = 33·15.

$C_8H_{18}OBrP$ requires C = 39·83; H = 7·47; Br = 33·15 per cent.

The phosphorus compounds have such an unpleasant odour that the work has had to be abandoned for some time.

The author has to thank Professor Letts and Professor Werner for their advice, and Professor Thompson for the facilities afforded to him for preparing some of the substances.

ROYAL COLLEGE OF SURGEONS IN IRELAND,
DUBLIN. [*Received, February 2nd*, 1916.]

XXXII.—*The Action of Sulphuric Acid on Alloy Steels.*

By Leslie Aitchison.

During the past few years a great many workers have been engaged on the investigation of the corrosion of various kinds of steel, and many others have been occupied with the constitution of the same steels, but up to the present very little has been done to try to correlate the two. It seems fairly obvious that it is not possible to obtain any very satisfactory explanation of the corrosion of steel unless the constitution is taken into account very closely, and it will be only when the dependence of the former phenomena on the latter is clearly understood and defined that a trustworthy theory of the corrosion of steels will be put forward. During the last three years the author has been endeavouring to ascertain the influence of composition on the corrosion of steels, and these results have already been published (*Trans. Faraday Soc.*, 1915, **11**). In the present work some effort has been made to find out how the constitution of the steels and the corrosion results are related. Much of our knowledge of the internal compositions of alloy steels is derived from those workers who have studied the carbides present in the steel, the most recent work having been done by Arnold and Read (*J. Iron Steel Inst.*, 1910, i, 169; 1911, i, 249; 1912, i, 215; *J. Mech. Engrs.*, 1914, i, 223; 1915, i, 247). These workers have shown the composition of the carbides that are found in these steels, their method of working being to separate the carbides by an electrolytic action. The composition of the remainder of the steel is to be inferred by difference, as they do not give any figures for the composition of the material which has passed into solution during the attack. Desch and Whyte have studied a similar method of working on a few steels containing either just iron and carbon or with manganese. In their case, however, the compositions given are those of the solution—showing what has been dissolved by the anodic action in the electrolytic cell.

The author has not followed either of these workers in their methods. He has accepted the values for the carbide compositions obtained by Arnold and Read. The method of working has been to treat the steels cold with 10 per cent. sulphuric acid for a limited time, and then to find the composition of the resulting solution. It can then be observed whether (as has been found by various other workers for iron carbide) the carbides are not attacked by this reagent or whether the corrosive action of this liquid results

in a decomposition of both the solid solution and the carbides. This information is of supreme importance in any study of corrosion, as it narrows the issue very much if only the solid solution is attacked. Assuming that corrosion is due to an ordinary kind of galvanic action, the constituents of the steel must be divisible into anodes and cathodes, and it seems fairly certain that if it can be shown that in such a powerful attack as that of 10 per cent. sulphuric acid the carbides are merely cathodic in their action and are not decomposed by the liquid, then in the milder attack by salt solutions or by tap water the assumption may be made very safely that the cathodes are immune from attack. Hence the problem of the production of a non-corrodible steel becomes that of the production of a practically non-corrodible alloy of iron and some other metal that enters into solid solution with it. The author has shown already that in the case of molybdenum steels the assumption that the carbides are immune from attack is an admissible one (T., 1915, **107**, 1531). In that case, there is no molybdenum to be found in the solution until the "saturation" point of the carbide as regards molybdenum is passed; hence the solid solution alone is the constituent that is acted on.

The present experiments were conducted as follows: Drillings of the steels in question were sieved carefully, and those separated that would pass through a ten-mesh, and not through a thirty-mesh, sieve. These drillings were weighed out in the quantities indicated below, and placed in graduated flasks with narrow necks. They were then treated for a specific time with a definite quantity of 10 per cent. sulphuric acid. The flasks and their contents were left in the cold during the whole operation. At the end of the time the contents of the flasks were filtered through hardened filter-paper in order to remove any of the undissolved drillings (which were always in excess), and also to catch the carbides which had been liberated during the progress of the action. Duplicate tests were made on all the samples. The clear filtrate from the drillings was then separated into two unequal fractions for the determination of the iron and the other metal that is desired. (In the case of the tungsten steels the whole of the solution was employed to estimate the tungsten, and the iron was determined in the filtrate from the tungstic oxide.) The results obtained and the analyses of the steels are given in the following tables. These also include the ratios of the second metal to the iron present in the solution, and also the ratios of the quantity of the second metal found in the solution to the quantity that should be present if the original ratio of iron to second metal in the steel had been preserved in the solution.

Vanadium Steels: Chemical Analysis.

No. of steel.	C. Per cent.	Si. Per cent.	Mn. Per cent.	S. Per cent.	P. Per cent.	V. Per cent.
1	0·11	0·034	0·19	0·018	0·020	0·17
2	0·38	0·038	0·28	0·020	0·022	0·22
3	0·73	0·036	0·33	0·019	0·021	0·21
4	0·96	0·040	0·36	0·016	0·020	0·20
5	1·30	0·035	0·31	0·019	0·021	0·21
6	0·60	0·050	0·06	0·041	0·010	0·71
7	0·63	0·090	0·07	0·042	0·011	2·32
8	0·93	0·21	0·11	0·039	0·018	5·84
9	1·07	0·32	0·12	0·041	0·030	10·30
10	1·10	0·47	0·12	0·040	0·031	13·45

Vanadium Steels: Four grams treated with 25 c.c. of 10 per cent. sulphuric acid for sixty minutes.

No. of steel.	V. Per cent.	Fe in solution. Gram.	V in solution. Gram.	Ratio. V : Fe.	Possible maximum of V in gram.*	Ratio of V found to V possible. Per cent.
1	0·17	0·451	—	—	0·0008	—
		0·417	—	—	0·0007	—
2	0·22	0·700	—	—	0·0015	—
		0·730	—	—	0·0016	—
3	0·21	0·467	—	—	0·0010	—
		0·480	—	—	0·0010	—
4	0·20	0·432	—	—	0·0009	—
		0·451	—	—	0·0009	—
5	0·21	0·845	—	—	0·0017	—
		0·823	—	—	0·0017	—
6	0·71	0·470	—	—	0·0034	—
		0·455	—	—	0·0033	—
7	2·32	0·590	—	—	0·0138	—
		0·593	—	—	0·0139	—
8	5·84	0·950	0·010	0·0105	0·0580	17·0
		0·920	0·010	0·0108	0·0573	17·4
9	10·30	0·935	0·033	0·0353	0·1670	31·0
		0·935	0·041	0·0435	0·1070	38·3
10	13·45	0·751	0·054	0·0718	0·1180	45·7

* This weight is calculated on the assumption that all the material corresponding with the iron found in solution has actually been dissolved. (This, of course, would involve the decomposition of the carbide.)

The vanadium steels show the utmost regularity in their behaviour. Arnold and Read showed (*J. Iron Steel Inst.*, 1912, i, 215) that vanadium replaces iron in the carbide of the steels in which it occurs, from the lowest percentages. The percentage of the possible vanadium actually found by these workers in their isolated carbides may be judged from the following table:

Vanadium in steel. Per cent.	Vanadium in dissolved part. Gram.	Vanadium in carbide. Gram.	Vanadium contained in carbide. Per cent.
0·71	0·0619	0·0583	94·4
2·32	0·184	0·0150	81·6*
5·84	0·499	0·420	84·3
10·30	0·875	0·492	56·2
13·45	1·136	0·595	52·2

* This result is probably much too low in view of the small yield of carbide as inferred from the percentage of carbon found as carbide in Arnold and Read's figures.

From this table the effect of the vanadium is to be found. Up to a certain composition the vanadium evidently is absorbed entirely by the carbide, and more finds its way into the solid solution. Beyond this percentage, vanadium is found in both carbide and solid solution. The "saturation" point for the steels of about the carbon employed in this investigation is roughly 5·4 per cent. of vanadium, and hence beyond this percentage the sulphuric acid solutions must show some vanadium. Referring to the results obtained with the acid, this is found to be true. In the steel with 5·84 per cent. of vanadium some of that element is found in the solution, and the amount present increases steadily with the further increase in the vanadium content of the steel. This seems to indicate quite clearly that the carbide is not attacked in any of the steels below the "saturation" point, and presumably from the figures, not in those above. Here, as in the molybdenum steels, the carbide appears to be immune from attack, and the solid solution only is dissolved by the sulphuric acid.

Chromium Steels: Chemical Analysis.

No. of steel.	C. Per cent.	Si. Per cent.	Mn. Per cent.	S. Per cent.	P. Per cent.	Cr. Per cent.
16	0·33	0·048	0·22	0·025	0·012	1·97
17	0·52	0·050	0·21	0·027	0·011	2·01
18	0·64	0·046	0·24	0·026	0·012	2·05
19	0·84	0·06	0·10	0·019	0·020	0·99
20	0·84	0·08	0·11	0·021	0·021	4·97
21	0·85	0·11	0·09	0·020	0·022	10·15
22	0·88	0·03	0·12	0·020	0·018	15·02
23	0·85	0·11	0·09	0·018	0·019	19·46
24	0·85	0·20	0·10	0·022	0·020	23·70

Chromium Steels: Five grams treated with 40 c.c. of 10 per cent. sulphuric acid for ninety minutes.

No. of steel.	Cr Per cent.	Fe in solution. Grams.	Cr in solution. Gram.	Ratio Cr : Fe.	Possible maximum of Cr. Gram.	Ratio of Cr found, to Cr possible. Per cent.
16	1·97	0·655	0·0069	0·0105	0·0129	53·5
		0·670	0·0067	0·0100	0·0132	50·8
17	2·01	0·383	0·0062	0·0165	0·0079	76·6
		0·379	0·0061	0·0164	0·0078	77·0
18	2·05	0·451	0·0069	0·0149	0·0091	76·0
		0·445	0·0075	0·0165	0·0089	83·0
19	0·99	0·337	0·0023	0·0068	0·0034	67·5
		0·313	0·0022	0·0070	0·0031	71·0
20	4·97	0·440	0·0123	0·0279	0·0230	53·5
		0·443	0·0120	0·0272	0·0233	51·5
21	10·15	0·463	0·0193	0·0417	0·0523	36·8
		0·474	0·0235	0·0492	0·0535	43·5
22	15·02	0·956	0·0975	0·1020	0·1693	57·5
		0·945	0·0938	0·0998	0·1670	56·2
23	19·46	1·44	0·1930	0·1335	0·3500	55·2
		1·41	0·1770	0·1259	0·3400	52·4
24	23·70	1·92	0·2620	0·1366	0·5950	44·2
		1·98	0·2800	0·1413	0·6160	45·3

In the chromium steels Arnold and Read (*J. Iron Steel Inst.*, 1911, i, 249) isolated the carbides from the bars that had been annealed at a bright red for some time, and they found that right from the start the chromium could be found in the carbide of the steel, the latter, hence, being a mixture of carbide of iron and chromium. An examination of their figures shows, however, that they did not obtain all the chromium present in the steel with the carbide, the mean proportion found being shown in the accompanying table:

Chromium in steel. Per cent.	Chromium in dissolved part.* Grams.	Chromium in carbide. Grams.	Chromium contained in carbide. Per cent.
0·65	0·065	0·036	55·2
0·99	0·0866	0·061	70·2
4·97	0·434	0·325	75·0
10·15	0·787	0·428	54·4
15·02	1·48	0·845	57·1
19·46	1·94	1·02	52·6

* The "dissolved part" includes the whole quantity of material removed from the test bars—that found in solution, and the residual carbide loosened by the solution of the matrix.

Evidently the chromium is to be found both in the solid solution and in the carbide. The results in the table, showing the acid attack, demonstrate the same fact, but indicate that there is more chromium found in the resulting solution than could be provided

by the solid solution alone in the steel. It may be assumed that the whole of the solid solution has been decomposed by the acid and a little of the carbide as well. In some cases the action on the carbide has been almost negligibly small—as in steel 21. Here the carbide takes 54·4 per cent., leaving 45·6 for the solid solution. In the latter, about 41 per cent. has been found by the acid action, the clear assumption being that the carbide is almost unattacked. In the steel 23 the carbide claims 52·6 per cent, leaving 47·4 per cent. for the solid solution. The acid attack finds 53·5 per cent., suggesting that the carbide has been attacked but slightly. In this case of chromium alloys the evidence tends to show that the carbides are attacked very slightly indeed, and in the higher ones (the non-corrodible members) almost negligibly.

Tungsten Steels: Chemical Analysis.

No. of steel.	C. Per cent.	Si. Per cent	Mn. Per cent.	S. Per cent.	P. Per cent.	W. Per cent.
25	0·20	0·48	0·08	0·048	0·012	3·22
26	0·58	0·080	0·08	0·052	0·011	3·16
27	0·88	0·040	0·09	0·041	0·010	3·07
28	1·08	0·038	0·08	0·041	0·012	3·11
29	0·74	0·107	0·15	0·025	0·016	2·36
30	0·72	0·107	0·16	0·023	0·015	5·37
31	0·70	0·037	0·13	0·021	0·014	9·74
32	0·74	0·032	0·14	0·026	0·014	14·96
33	0·73	0·063	0·15	0·024	0·016	21·15
34	0·68	0·061	0·15	0·025	0·017	26·3

Tungsten Steels: Five grams treated with 40 c.c. of 10 per cent. sulphuric acid for two hundred and seventy minutes.

No. of steel.	W. Per cent.	Fe in solution. Grams.	W. in solution. Grams.	Ratio W : Fe.	Possible maximum of W. Gram.	Ratio of W found to W possible. Per cent.
25	3·22	0·478	0·008	0·0168	0·0155	51·5
		0·482	0·0072	0·0151	0·0156	46·2
26	3·16	1·00	0·0048	0·0048	0·0316	15·3
		1·02	0·0064	0·0062	0·0318	20·3
27	3·07	1·108	0·0028	0·0025	0·0342	8·25
		1·104	0·0022	0·0020	0·0340	6·45
28	3·11	1·42	0·0026	0·0018	0·0440	5·91
		1·41	0·0024	0·0017	0·0437	5·50
29	2·36	1·58	—	—	0·0367	—
		1·58	—	—	0·0367	—
30	5·37	1·80	—	—	0·102	—
		1·75	—	—	0·100	—
31	9·74	1·70	—	—	0·184	—
		1·73	—	—	0·187	—
32	14·96	1·23	0·0032	0·0026	0·217	1·47
		1·24	0·0029	0·0023	0·218	1·33
33	21·15	1·16	0·0069	0·0059	0·318	2·17
		1·11	0·0069	0·0062	0·304	2·26
34	26·3	1·38	0·0128	0·0093	0·495	2·58

For the tungsten alloys the carbide residue has been found to be peculiar, in that after a certain "saturation" percentage has been reached the carbide isolated is accompanied by some excess of iron and tungsten. Hence it might be expected that the solid solution should be relatively free from tungsten during the greater part of the series. The results obtained by Arnold and Read are embodied in the following table:

Tungsten in steel. Per cent.	Tungsten in dissolved part. Grams.	Tungsten in isolated carbide. Grams.	Tungsten associated with carbide. Per cent.
2·36	0·179	0·159	88·7
5·37	0·435	0·410	94·2
9·74	0·786	0·763	96·6
14·96	0·936	0·633	67·6
21·15	1·613	1·262	78·3
26·29	1·710	1·140	66·5

These figures were obtained with steels that had been annealed for some little time, whilst the author's series of corresponding compositions (steels 29 to 34) were treated more tenderly—having been normalised only. As a result, some divergence might be expected. It may be seen, however, that this divergence is not serious, as no tungsten at all occurs in the sulphuric acid solutions until after the "saturation" point has been passed, this occurring according to Arnold and Read at about 11·5 per cent. of tungsten. It is fairly evident that in this series, as in the previous one, there is no attack on the carbide throughout the series. The presence of some tungsten in the solutions obtained from the steels of low carbon content is interesting, and suggests that relatively slight variations in the heat-treatment of the tungsten steels may produce a distinct variation in the constitution of these steels. The presence of the tungsten may be accounted for by the lack of carbon in the steels of low carbon content, as the percentage of tungsten found in the solid solution falls rapidly with an increase in the percentage of carbon.

The variation in the behaviour of steels 25 to 28 with the acid, from that of steels 29 to 34 is instructive also in view of the peculiarity in the corrosion of these two series of steels. In general, the members of the first-mentioned series corrode less than those of the second, and no apparent reason was forthcoming until the probable percentage of tungsten in the solid solution was shown. It will be seen also that in these acid experiments on the whole the members of the series 29 to 34 have lost less material to the acid than have the higher tungsten steels.

Nickel Steels: Chemical Analysis.

No. of steel.	C. Per cent.	Si. Per cent.	Mn. Per cent.	S. Per cent.	P. Per cent.	Ni. Per cent.
35	0·07	0·043	0·13	0·013	0·014	3·07
36	0·28	0·049	0·14	0·014	0·016	3·13
37	0·48	0·046	0·14	0·012	0·015	2·94
38	0·76	0·050	0·19	0·012	0·015	3·08
39	0·88	0·042	0·18	0·011	0·016	2·97

Nickel Steels: Five grams treated with 40 c.c. of 10 per cent. sulphuric acid for two hundred and twenty-five minutes.

No. of steel.	Ni. Per cent.	Fe in solution. Gram.	Ni in solution. Gram.	Ratio Ni : Fe.	Possible maximum of Ni. Gram.	Ratio of Ni found to Ni possible. Per cent.
35	3·07	0·498	0·0151	0·0304	0·0159	95·5
		0·540	0·0161	0·0298	0·0170	94·9
36	3·13	0·575	0·0181	0·0315	0·0183	98·8
		0·602	0·0185	0·0307	0·0190	97·7
37	2·94	0·681	0·0193	0·0284	0·0204	94·5
		0·710	0·0213	0·0300	0·0214	99·7
38	3·08	0·471	0·0149	0·0315	0·0147	101·8
		0·459	0·0148	0·0322	0·0143	103·3
39	2·97	0·795	0·0263	0·0330	0·0241	108·2
		0·983	0·0322	0·0322	0·0301	107·0

The results with the nickel steels are of some interest. Arnold and Read have shown that nickel is not found as a constituent of the carbide with percentages less than 8·0, and hence, as in the series used above, the percentage of nickel is only 3, all of it should be found in the solid solution. That this is so may be seen from the ratio of iron to nickel in the solution. Whether the carbide has been attacked or not is not quite so easy to decide. As the carbon in the steel rises, more and more iron is required to combine with it to form the carbide. Hence the concentration of the solid solution as regards nickel should rise. The acid solution should reflect this if the carbide is unattacked. That this is what actually occurs may be seen from the last column of the previous table, as the "nickel possible" is calculated on the ground that the carbide is decomposed. Hence the evidence, whilst not conclusive, points to the fact that here, as in the other steels, the carbide is not attacked during the solution of the rest of the metal.

Cobalt Steels: Chemical Analysis.

No. of steel.	C. Per cent.	Si. Per cent.	Mn. Per cent.	S. Per cent.	P. Per cent.	Co. Per cent.
11	0·73	0·05	0·16	Less than 0·04	Less than 0·02	2·68
12	0·65	0·07	0·18			5·50
13	0·75	0·09	0·23			11·18
14	0·75	0·10	0·23			16·97
15	0·72	0·11	0·25			20·85

Cobalt Steels: Five grams treated with 40 c.c. of 10 per cent. sulphuric acid for one hundred minutes.

No. of steel.	Co. Per cent.	Fe in solution. Gram.	Co in solution. Gram.	Ratio. Co : Fe.	Possible maximum of Co. Gram.	Ratio of Co found to Co possible. Per cent.
11	2·68	0·340	—	—	0·0091	—
		0·340	—	—	0·0091	—
12	5·50	0·313	trace	trace	0·0182	trace
		0·315	trace	trace	0·0182	trace
13	11·18	0·595	0·064	0·107	0·0748	85·5
		0·583	0·065	0·102	0·0735	88·0
14	16·97	0·547	0·104	0·191	0·1118	93·0
		0·513	0·102	0·198	0·1060	96·0
15	20·85	0·745	0·190	0·255	0·1960	96·5
		0·730	0·190	0·260	0·1930	98·0

The results obtained with the cobalt alloys are unfortunately incomplete in consequence of the fact that the heat treatment of the samples has resulted in the partial decomposition of the members containing more cobalt. These steels have allowed their carbide to decompose to a greater or less extent, and have precipitated graphite, and so allowed any cobalt they possessed to pass into the solid solution. The results obtained by Arnold and Read (*J. Inst. Mech. Engrs.*, 1915, 1) show that the percentage of cobalt in the carbide rises with the percentage of cobalt present in the steels. The figures obtained by the author show that there is no cobalt at all in the solutions from the lowest cobalt steel, and that as soon as the higher ones are reached and graphite has been precipitated, there is found the whole of the cobalt, or almost the whole of it. The suggestion from the figures on the steels of lower cobalt content is that the cobalt is bound up with the carbide and is unattacked by the acid, this being in accordance with the other series of steels.

Manganese Steels: Chemical Analysis.

No. of steel.	C. Per cent.	Si. Per cent.	Mn. Per cent.	S. Per cent.	P. Per cent.
40	0·28	0·030	0·94	0·042	0·037
41	0·48	0·028	0·91	0·043	0·038
42	0·69	0·11	0·92	0·048	0·050
43	0·76	0·078	0·83	0·041	0·019
44	0·87	0·035	1·01	0·037	0·034

Manganese Steels: Five grams treated with 40 *c.c. of* 10 *per cent. sulphuric acid for seventy minutes.*

No. of steel.	Mn. Per cent.	Fe in solution. Grams.	Mn in solution. Gram.	Ratio Mn : Fe.	Possible maximum of Mn. Gram.	Ratio of Mn found. to Mn possible. Per cent.
40	0·94	1·251	0·0073	0·0058	0·0117	62·5
		1·271	0·0080	0·0063	0·0119	67·2
41	0·91	0·94	0·0063	0·0067	0·0085	74·0
		0·955	0·0058	0·0061	0·0087	67·0
42	0·92	0·575	0·0045	0·0078	0·0053	85·0
		0·603	0·0045	0·0075	0·0055	82·0
43	0·83	0·980	0·0058	0·0059	0·0081	71·5
		0·830	0·0059	0·0071	0·0069	85·0
44	1·01	0·56	0·0049	0·0087	0·0057	85·8
		0·61	0·0051	0·0084	0·0062	82·5

The manganese alloys are not very extensive in range, but are near the compositions that are met in ordinary practice. The variation in carbon is interesting, however. Arnold and Read (*J. Iron Steel Inst.*, 1910, i, 169) have shown that there is an entrance of manganese into the carbides at quite low percentages—in fact, from the lowest that was examined. With an increase of manganese in the steel there was a regular increase in the proportion found in the carbide. The figures for the compositions near to those employed by the author are as follows:

Manganese in steel. Per cent.	Manganese in dissolved part. Gram.	Manganese in carbide. Gram.	Manganese associated with the carbides. Per cent.
0·41	0·0183	0·0106	57·6
0·83	0·0371	0·0216	58·2
1·16	0·0479	0·0271	56·6

The figures obtained for the action of acid on these steels suggest that in the steels of low carbon content there may not be an action on the carbides, but in those of the higher carbon content there is a definite attack. This is not surprising when the corrosion tests on these steels are considered, and also when the nature of the carbides is taken into account. The carbide is present chiefly in a very fine (sorbitic) form, and certainly presents every possibility for the action if it is possible to take place. In this series of steels it seems fairly certain that there has been some decomposition of the carbide.

Considering the above results, it becomes reasonably certain that the majority of the carbides found in alloy steels are not susceptible to the attack of dilute sulphuric acid. This is more definitely true of those steels containing the larger proportions of the third

added element. In all probability these carbides have a much greater chemical stability than has the pure carbide of iron which is present in plain carbon steels. As they are not decomposed by this powerful corrosive, it is surely a reasonable inference that the milder corrosive agents—like tap-water and brine—will be without action on the carbides. This result is quite in accordance with the results obtained by a microscopic examination of these steels before and after corrosion. In consequence, the issue for the producer of a rustless alloy is narrowed down to a consideration of the solid solution only. If the action is a galvanic one, the carbides must be acting as cathodes to the anodes of the solid solution. The carbides are likely to be of very similar electrical potential whatever their composition, and hence the action will depend very largely on the potential of the solid solutions. The lower that these can be made, then the less the corrosion.

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XXXIII.—*The Vapour Pressure of Glyceryl Trinitrate (Nitroglycerin).*

By ARTHUR MARSHALL and GORDON PEACE.

IN 1904 one of us made a rough estimation of the vapour pressure of glyceryl trinitrate (Marshall, *J. Soc. Chem. Ind.*, 1904, **23**, 158), which at 70° was found to be approximately the same as that of mercury. In spite of the commercial importance of nitroglycerin and the trouble caused by its volatility, this remained until recently the only available measurement of its vapour tension. In 1913, having occasion to calculate the partial pressure curve of glyceryl trinitrate in acetone solution at 18° it was assumed, in order to be able to draw the curve on a definite scale, that at this temperature also the vapour pressure is approximately the same as that of mercury, namely, 0·001 mm. of mercury (P., 1913, **29**, 157).

The vapour pressure was estimated by bubbling a known volume of air through nitroglycerin contained in a small flask and determining its loss of weight, as also the gain of weight of a condenser tube. Chiaraviglia and Corbino (*Gazzetta*, 1913, **43**, ii, 390) have impugned the accuracy of the estimation. They contend that, on the one hand, the air may have carried away mechanically globules

of glyceryl trinitrate, and on the other that the air may not have been fully saturated with the vapour. They have also attempted to determine the vapour pressure at the ordinary temperature by an entirely different method, depending on the fact that in a high vacuum the rate of cooling of a hot body is a function of the concentration of the gaseous molecules present. A small vessel containing the bulb of a thermometer was exhausted by means of a Gaede pump in the presence of glyceryl trinitrate. It was heated to about 50°, then immersed in cold water, and an observation was made of the time required for the temperature to fall from 50° to 30°. Determinations were made with the vessel filled with air at pressures varying from 0·0005 to 0·002 mm. both in the presence and absence of glyceryl trinitrate. No perceptible difference in the rate of fall of temperature was caused by the presence of the trinitrate during the preparation of the vessel. Hence the authors draw the deduction that the vapour pressure of nitroglycerin at the ordinary temperature is less than 0·0001 mm. of mercury. Unfortunately the experiments were made in the presence of phosphoric oxide, and Chiaraviglia and Corbino entirely overlooked the fact that this substance absorbs the vapour of glyceryl trinitrate rapidly and completely. Consequently, the deduction they have drawn from their experiments is unsound.

The determination of the vapour pressure of glyceryl trinitrate appeared to merit further investigation. Measurements have therefore been made by a method that is substantially the same as that used by Marshall in 1904, but instead of bubbling air through the liquid trinitrate it was passed through a tube containing powdered cordite. In this way the two sources of error suggested by Chiaraviglia and Corbino are entirely avoided. As the area of cordite exposed is enormous, the air must be saturated completely, and no spray of the liquid can be formed. It may be objected that the vapour pressure of the trinitrate in the cordite is not necessarily the same as that of the pure substance. The composition of cordite Mark I is:

Guncotton	37
Nitroglycerin	58
Mineral jelly	5

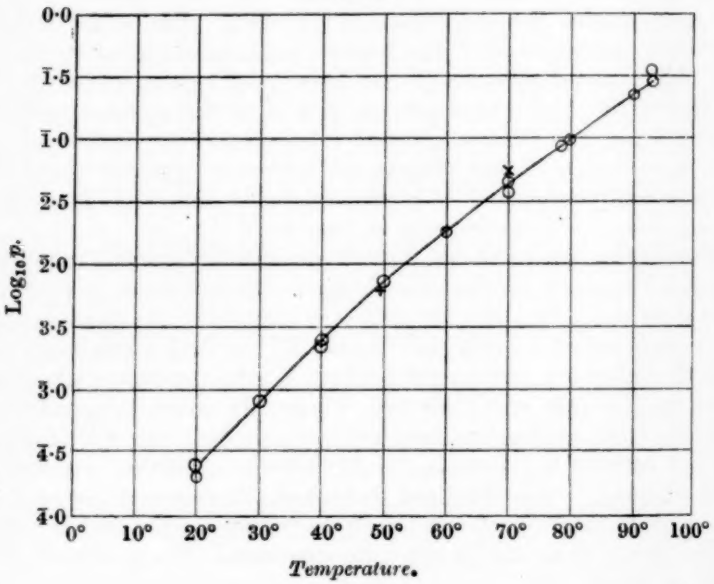
The other two constituents are almost insoluble in nitroglycerin and they are of high molecular weight, and, moreover, guncotton is a colloid. Hence they should not affect the vapour pressure appreciably. Further, Chiaraviglia and Corbino have found that in a high vacuum saturated with vapour of the trinitrate structureless nitrocotton only absorbs 1·8 per cent. (*Atti R. Accad. Lincei*, 1915, **24**, 250), which shows that when more than 2 per cent. of glyceryl

trinitrate is present the vapour tension is almost the same as that of the pure liquid. Our determinations are in good agreement with that made previously with liquid glyceryl trinitrate and a new determination with cordite M.D. which has the composition:

Guncotton	65
Nitroglycerin	30
Mineral jelly	5

The arrangement of the apparatus was as follows: The air first passed through two U-tubes filled with calcium chloride, then through a U-tube immersed in a thermostat and containing about 30 grams of ground cordite prepared as for the Abel heat test and thoroughly dried. From this the air passed through a condensing

FIG. 1.



tube, which was simply a glass tube bent so that part of it could be immersed in a cooling liquid. A small wad of glass-wool was inserted at the end where the air entered, to afford extra surface for condensation and to prevent particles falling out. Another wad of glass-wool was placed in the bent portion. During the determinations at low temperatures the bent portion was kept at or below 0°.

From this tube the air passed to a wash-bottle containing sulphuric acid and then to a gas-holder, which served as an aspirator and also to measure the volume of air drawn through.

The vapour pressure is calculated from the equation:

$$p = \frac{32 \times T \times W \times 760}{1{\cdot}429 \times 273 \times 227 \times V} = 0{\cdot}02746\,\frac{TW}{V}.$$

where p is the vapour pressure in mm. of mercury.

W is the weight of glyceryl trinitrate condensed in grams.

V is the volume of air drawn through measured in litres at absolute temperature T and corrected for moisture.

1·429 is the weight of a litre of oxygen at 273° absolute and 760 mm.

32 and 227 are the molecular weights of oxygen and glyceryl trinitrate respectively.

The following were the results obtained:

Temperature of thermostat.	Temperature of gas-holder. T–273.	Volume of air. Litres. V.	Glyceryl trinitrate condensed. Grams. W.	Log · $_{10}$ Vapour pressure.	Vapour pressure in mm. p.
20·0°	19·0°	182·0	0·0006	$\bar{4}$·41	0·00026
20·0	20·4	200·0	0·0006	$\bar{4}$·38	0·00024
30·0	21·0	29·1	0·0003	$\bar{4}$·92	0·00083
40·0	21·1	28·7	0.0009	$\bar{3}$·40	0·0025
40·0	23·0	27·8	0·0008	$\bar{3}$·37	0·0023
50·0	21·25	27·9	0·0025	$\bar{3}$·86	0·0072
50·0	20·5	28·7	0·0026	$\bar{3}$·86	0·0073
60 0	21·75	28·8	0·0067	$\bar{2}$·27	0·0188
70·0	22·0	13·3	0·0073	$\bar{2}$·65	0·044
70·0	22·0	15·0	0·0078	$\bar{2}$·63	0·042
79·6	22·0	14·6	0·0170	$\bar{2}$·97	0·094
80·0	25·0	10·9	0·0131	$\bar{2}$·99	0·098
90·0	25·0	7·68	0·0218	$\bar{1}$·37	0·235
90·0	22·5	7·32	0·0203	$\bar{1}$·35	0·225
93·4	21·0	28·3	0·1104	$\bar{1}$·50	0·31
93·3	22·0	14·1	0·0504	1·46	0·29
		Cordite M.D.			
49·7	21·5	28·6	0·0024	$\bar{3}$·83	0·0068
		Liquid Nitroglycerin.			
70·0	13·5	1·82	0·0011	$\bar{2}$·68	0·047

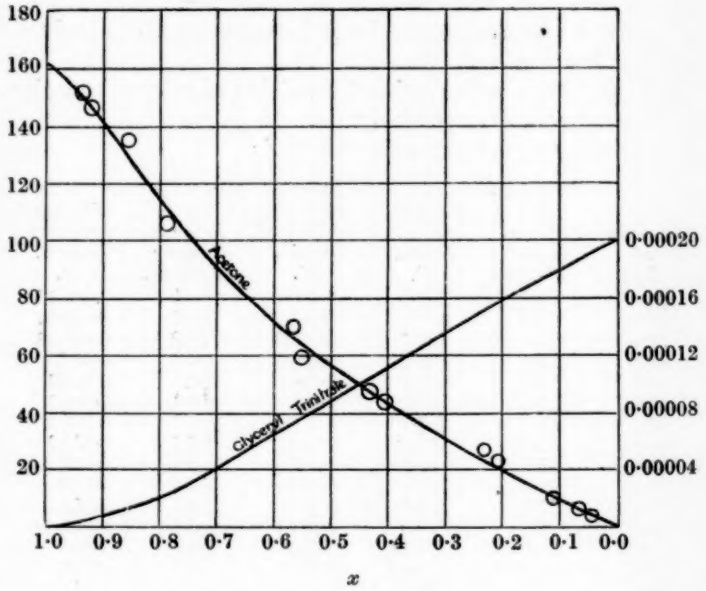
At the higher temperatures, 90° and above, the results are possibly too high as the nitroglycerin decomposes at an appreciable rate at these temperatures, even in the presence of mineral jelly, forming glyceryl dinitrate and other volatile products, which may have condensed in the tube.

The rate of rise of the logarithm of the vapour pressure is of the same order as in the case of some other organic compounds, but is considerably greater than in the case of mercury. At 20° the vapour pressure is about 0·0002, not 0·001 as was previously assumed (P.,

1913, **29**, 157) when calculating the partial pressure curve of nitroglycerin in acetone solution. This difference in no way affects the shape of the curve, but the figures in the fourth and fifth columns of the table there given require to be multiplied throughout by the

FIG. 2.

Partial pressure curves at 18°.



factor 0·2. The table is given below with this correction carried out:

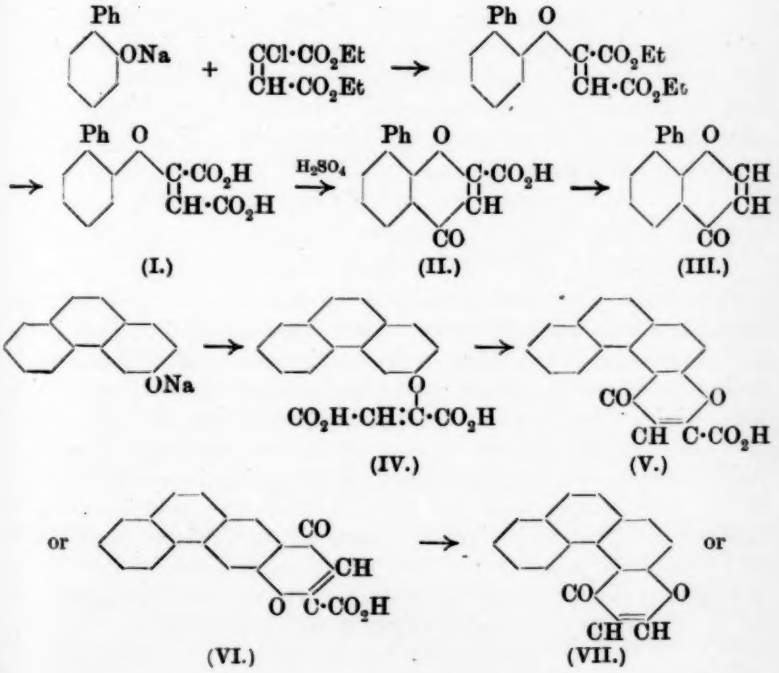
x (acetone).	p_1 (acetone.)	dp_1/dx.	$p_2 . 10^6$ (glyceryl trinitrate.	$-dp_2/dx . 10^6$.	Glyceryl trinitrate in liquid phase. Per cent.
0·0	0·0	—	200	200	100·0
0·1	8·2	90	179	218	97·2
0·2	18·4	106	157	226	94·0
0·3	29·5	116	134	226	90·1
0·4	41·5	131	111	234	85·4
0·5	55·7	149	88	234	79·7
0·6	71·3	171	63	226	72·3
0·7	90·0	205	41	216	62·6
0·8	112·2	255	20	186	49·4
0·9	141·0	280	6	144	30·3
1·0	162·0	162	0	—	0·0

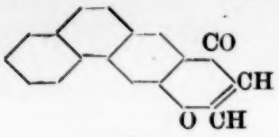
[*Received, January 7th*, 1916.]

XXXIV.—*Synthesis of 8-Phenyl-γ-benzopyrone and a γ-Phenanthropyrone.*

By Amy Rose Watson.

The present investigation was undertaken to test the view that pyrone compounds are capable of forming blue additive compounds with iodine resembling the so-called iodide of starch (Barger and Starling, T., 1915, **107**, 411), and that their affinity to iodine increases with the number of benzene rings in the molecule. For this purpose the convenient chromone synthesis of Ruhemann (T., 1901, **79**, 470) was applied to 2-hydroxydiphenyl and to 3-phenanthrol. By condensing the sodium derivatives of these phenols with ethyl chlorofumarate, the ethyl esters of 2-diphenylyloxyfumaric (I) and of 3-phenanthroxyfumaric (IV) acids were obtained; by dehydration of these acids with sulphuric acid and with phosphoric oxide there resulted carboxylic acids of the required pyrone derivatives (II and V or VI), from which the pyrones themselves (III and VII or VIII) were obtained by distillation under diminished pressure. The reactions involved are represented as follows:





(VIII.)

In the case of the phenanthrene derivatives the constitution of the pyronecarboxylic acid and of the pyrone remains doubtful, because the linking may take place in positions 2 or 4. A similar doubt arises in the case of β-naphthaflavone (Ruhemann, *Ber.*, 1914, **47**, 122), who favours a constitution corresponding with formulæ V and VII.

Experimental.

Ethyl 2-Diphenylyloxyfumarate.

Ten grams of 2-hydroxydiphenyl were melted with one equivalent of sodium, and the mixture was then heated with one equivalent of ethyl chlorofumarate for a short time under a reflux condenser. The product was extracted with ether, and after washing with sodium hydroxide, acetic acid, and water, the ethereal solution was dried and evaporated. On distillation under 2 mm. pressure three fractions were isolated, boiling at 160—180°, 180—194°, and above 200°. The middle fraction, a pale yellow, viscid liquid, consisted principally of the required ester, but since analysis showed it to be still very impure, it was hydrolysed, the resulting acid was recrystallised, and again esterified with alcohol and hydrogen chloride. The ester then had an almost constant boiling point of 185°/2 mm.:

0·0910 gave 0·2344 CO_2 and 0·0425 H_2O. C = 70·0; H = 5·2.

$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

2-Diphenylyloxyfumaric Acid.

The crude ester was hydrolysed by boiling for an hour with alcoholic potassium hydroxide. After removal of the alcohol, the acid was precipitated with hydrochloric acid, and redissolved in sodium carbonate, some unchanged 2-hydroxydiphenyl being removed by filtration. On acidifying the solution, the acid separated as a cream-coloured, curdy precipitate, sparingly soluble in boiling water. It was crystallised by dissolving in alcohol, adding water, and evaporating the alcohol until the solution became opalescent. The acid formed cream-coloured prisms melting at 210°, the yield being 70 per cent. of the theoretical:

0·0969 gave 0·2457 CO_2 and 0·0349 H_2O. C = 67·2; H = 4·0.

$C_{16}H_{12}O_5$ requires C = 67·6; H = 4·2 per cent.

8-Phenyl-γ-benzopyrone-2-carboxylic Acid.

Seven grams of 2-diphenylyloxyfumaric acid were dissolved in concentrated sulphuric acid, and after a day the solution was poured on ice and the precipitate crystallised in the same way as the previous substance. The new acid crystallised in pale yellow needles, melting at 249°, and subliming unchanged under 2 mm. pressure (bath at 250°). The yield was only 1·5 grams, or 23 per cent. of the theoretical. The loss appeared to be due to the formation of soluble sulphonic acids:

0·1178 gave 0·3107 CO_2 and 0·0407 H_2O. C = 71·9; H = 3·8.

$C_{16}H_{10}O_4$ requires C = 72·2; H = 4·1 per cent.

The *ethyl* ester of the above acid was prepared in the usual way with alcohol and hydrogen chloride; as the reaction proceeded, an intense reddish-green fluorescence was developed. The solution left on evaporation a green, crystalline residue, which after two crystallisations from alcohol yielded yellow needles melting at 133°:

0·1272 gave 0·3420 CO_2 and 0·0529 H_2O. C = 73·4; H = 4·6.

$C_{18}H_{14}O_4$ requires C = 73·5; H = 4·8 per cent.

8-Phenyl-γ-benzopyrone.

As the pyronecarboxylic acid sublimed unchanged under a pressure of 2 mm., the elimination of carbon dioxide was effected by heating small quantities in test-tubes in a metal bath at 270° under a pressure of 20—30 mm. The pale yellow distillate solidified on cooling, and was dissolved in boiling alcohol. On adding water and evaporating the excess of alcohol, the pyrone crystallised in long, colourless needles melting at 112°:

0·0952 gave 0·2826 CO_2 and 0·0358 H_2O. C = 81·0; H = 4·2.

$C_{15}H_{10}O_2$ requires C = 81·1; H = 4·5 per cent.

8-Phenyl-γ-benzopyrone differs from flavone (2-phenyl-γ-benzopyrone) in not fluorescing in concentrated sulphuric acid solution under conditions when flavone gives a very marked fluorescence. Its basic properties are indicated by the formation of a yellow, crystalline *platinichloride*, which, however, dissociates very easily in alcoholic solution.

3-Phenanthroxyfumaric Acid.

Owing to the high melting point of 3-phenanthrol it was found inconvenient to prepare its sodium derivative by melting the constituents together. Instead, the phenanthrol was treated in alcoholic solution with an equivalent of sodium ethoxide, and the alcohol was then removed by distillation under diminished pressure, finally

at 180°. The dry sodium salt was treated in toluene suspension with one equivalent of ethyl chlorofumarate; after boiling for a short time under reflux, the solid sodium derivative disappeared, when the toluene solution was diluted with ether, washed with water, dried, and evaporated. The viscous residue distilled at 210—220°/2 mm., and was at once hydrolysed with alcoholic potassium hydroxide. After purification from unchanged phenanthrol by means of sodium carbonate, 0·4 gram of a yellow acid melting at 208° was obtained. This small yield was the result of heating the sodium salt of phenanthrol to 180°, for in a second experiment, when the alcohol was removed at 100°, the yield of the phenanthroxyfumaric acid amounted to nearly 50 per cent. of the theoretical, and the product appeared to be much purer. The acid could not be obtained in well-defined crystals, but by slowly cooling its solution in glacial acetic acid the melting point was raised to 223°, and remained constant after a second dissolution:

0·1002 gave 0·2575 CO_2 and 0·0331 H_2O. C = 70·1; H = 3·7.
$C_{18}H_{12}O_5$ requires C = 70·1; H = 3·9 per cent.

γ-Phenanthropyrone.

The elimination of water from 3-phenanthroxyfumaric acid was accomplished by means of phosphoric oxide. 3-Phenanthroxyfumaric acid (0·9 gram) and phosphoric oxide (3·35 grams) were heated for two to three hours in benzene suspension. On pouring into water and distilling off the benzene the product was found to give a blue coloration with iodine, but the yield was poor. Somewhat better results were obtained with boiling xylene, but in no case could the phenanthropyronecarboxylic acid be crystallised, so it was distilled under 2 mm. pressure in small test-tubes from a bath at 270—280°. There was considerable decomposition. The distillate was dissolved by means of alcohol, precipitated by water, extracted with ether, and washed with sodium carbonate. The residue left on evaporation of the ether crystallised from a mixture of benzene and light petroleum in clusters of needles melting at 162—164°. The amount so obtained was too small for macro-analysis, but from the fact that the substance gave the characteristic pyrone reaction with iodine, and from the method of its formation, its composition can scarcely be in doubt.

Attempts at removing water from the acid by means of sulphuric acid, and hydrogen chloride from the acid chloride by means of aluminium chloride, were unsuccessful.

Reaction of the above Pyrone Compounds with Iodine.

8-Phenyl-γ-benzopyrone-2-carboxylic acid dissolved in alkali gives an intense blue coloration when poured into $N/100$-potassium triiodide solution containing excess of acid. An alcoholic solution of its ethyl ester behaves similarly. 8-Phenyl-γ-benzopyrone itself is much more sensitive, giving a blue adsorption compound with iodine up to a dilution of $N/4000$, the same limit as that for the isomeric substance flavone (T., 1915, **107**, 420).

γ-Phenanthropyrone in 1 per cent. alcoholic solution gave a blue coloration with aqueous iodine solutions up to $N/2000$. This is intermediate between the limits for the two naphthaflavones, which also contain three benzene rings in addition to the pyrone ring, the α-compound being twenty to thirty times as sensitive ($N/40{,}000$—$N/60{,}000$). It would be of interest to examine pyrones derived from 1- and 4-phenanthrol, which might be expected to show a greater affinity for iodine.

In conclusion, I wish to thank Professor G. Barger for suggesting this work, and for constant help and encouragement during its progress; the materials were purchased by the aid of a grant made to him from the Research Fund of the Chemical Society, of which grateful acknowledgment is made.

Royal Holloway College,
Englefield Green, Surrey. [*Received, March 9th*, 1916.]

XXXV.—*The Acid–Gelatin Equilibrium.*

By Henry Richardson Procter and John Arthur Wilson.

In an earlier paper by one of us (T., 1914, **105**, 313) it was shown that gelatin forms hydrolysable salts with acids, that swelling is due to the ionisation of these and the osmotic pressure so produced, and that an equilibrium results, in which the concentrations of anion, hydrion, and ionised gelatin salt can all be expressed as functions of the concentration of acid in the external solution, within the limits of experimental error. In this earlier paper the concentration of the ionised gelatin chloride in the equilibrium gelatin–hydrochloric acid was shown to be approximately $Cl_g = \sqrt{0{\cdot}02x + 0{\cdot}0002}$, where Cl_g was the chlorine ionised from the gelatin salt, and x the concentration, in terms of normality, of the external hydrochloric acid. (Through an error Cl_g was given

as $\sqrt{2x+0{\cdot}02}$, but all actual calculations were made from the above formula.) It was also assumed that the numerical values in the expression were constants, as those adopted sufficiently closely represented the experimental results then quoted, but closer theoretical investigation has shown that this is not strictly the case, but that both Cl_g and x are functions of a quantity e, which is the difference in osmotic pressure between two phases of which the ionic products are equal, but in one of which the factors are unequal; and that it is this difference which causes the swelling of the jelly.

In the paper cited the hydrochloric acid and gelatin salt were for the sake of simplicity supposed to be wholly ionised, and as the ionisation in both cases is very high and the solutions were dilute, such an assumption was quite justifiable as regards experimental results. In the closer theoretical examination which we now propose, however, we must define the concentrations as referring only to the actual ions; and we shall again first consider the comparatively simple case of hydrochloric acid and gelatin, where the ionisation is in reality almost complete.

The following system of notation will be employed:

At equilibrium:

in the external solution:

$x=[H^+]=[Cl']$.

in the jelly phase:

$y=[H^+]$.

$z=$concentration of gelatin ions.

$y+z=[Cl']$.

$a=$concentration of non-ionised gelatin chloride.

$g=$sum of concentrations of gelatin, gelatin chloride, and gelatin ions.

$e=$excess of concentration of diffusible ions of the jelly over that of the external solution.

$V=$volume of the jelly in c.c.

All concentrations are expressed in gram-equivalents per litre. In all experiments 1 gram of dry gelatin was immersed in 100 c.c. of the acid solution and allowed to remain for forty-eight hours to reach equilibrium, the temperature being about 20° in each case. The concentration of acid in the external solution was determined by titration, and that in the jelly by titrating the solution expelled from the jelly by the addition of salt, and with these, knowing the initial concentration of the acid and the percentage of ionisation of acid in the external solution, the actual ionic concentrations can be calculated.

In a two-phased equilibrium, such as the present, two different equations must be fulfilled. It is necessary that the products of hydrion and chloridion should be equal in the two phases; that is:

$$x^2 = y(y+z) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This is not only proved by the thermodynamical equation of Donnan, quoted in the earlier paper (*loc. cit.*), but also follows from the ordinary laws of ionisation, since the non-ionised portion of hydrochloric acid which, although small, must exist, takes no direct part in the equilibrium, and must be equal in both phases since the jelly is permeable to it, and

$$x^2 = [H_1^+] \times [Cl'_1] = K[HCl] = [H_2^+] \times [Cl'_2] = y(y+z).$$

It was, however, previously pointed out that the equations

$$\begin{cases} x^2 = y(y+z) \\ 2x = 2y+z \end{cases}$$

cannot simultaneously be fulfilled, since in the jelly $[H^+]$ and $[Cl']$ are necessarily unequal, the chloridion being greater than the hydrion by the amount z, and the sum of the sides of an unequal rectangle is necessarily greater than that of the sides of a square of equal area (see Fig. 1). In other words, $2y+z$ is greater than $2x$ by an amount we shall call e, and the corrected equation becomes:

$$2x+e = 2y+z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The concentration of diffusible ions of the jelly is therefore greater by e than that of the outer solution. It is obvious, since water and hydrogen chloride can pass freely into the jelly, that there must be some force equal to and opposing the osmotic pressure produced by this excess e of concentration at equilibrium, for otherwise the jelly would tend to swell to infinity.

Before attempting to speculate about the nature of this opposing force, we must consider its mathematical relations to the other concentrations of the equilibrium as defined by equations (1) and (2). The general theory of the equilibrium as developed in earlier papers (*Koll.-chem. Beihefte*, 1911, **2**, 243, and T., *loc. cit.*) is that when gelatin is placed in dilute acid it absorbs it freely and forms a hydrolysing salt, the proportion of which to the whole gelatin-base present is determined by the hydrolysis equation. The gelatin salt, like other salts, is highly ionised into the anion and a colloid cation, which either from polymerisation or other causes peculiar to the colloid state cannot diffuse and exerts no measurable osmotic pressure, whilst its anion is retained in the jelly by the electrochemical attraction of the colloid ion, but exerts osmotic pressure which, on the one hand, causes the mass to swell with absorption of the external solution, and, on the other, expels a portion of the

acid, both anion and hydrion, from this solution absorbed, the result in equilibrium being that the jelly is poorer in hydrion and more concentrated in anion than the external acid solution, the difference of concentration between anion and hydrion in the jelly being, of course, equal to the ionised anion of the gelatin salt, and electrically balanced by the positive gelatin ions; whilst the hydrion concentration in the jelly is less than that of the outer solution by the amount of acid expelled, which may be called v (the isotonic volume of hydrion or chloridion expelled at a concentration of x); v bears the simple relation to y that $y+v=x$ and the concentration of ionised gelatin chloride, $z=2v+e$.

By solving simultaneously equations (1) and (2) the following interesting relations are derived:

$$x=y+\sqrt{ey}=\sqrt{y^2+yz}=\frac{z^2-e^2}{4e}$$

$$y=\frac{-z+\sqrt{z^2+4x^2}}{2}=\frac{2x+e-\sqrt{4ex+e^2}}{2}=\frac{(z-e)^2}{4e}$$

$$z=\frac{x^2-y^2}{y}=\sqrt{4ex+e^2}=e+2\sqrt{ey}$$

$$e=\frac{(x-y)^2}{y}=z+2y-2\sqrt{y^2+yz}=-2x+\sqrt{4x^2+z^2}$$

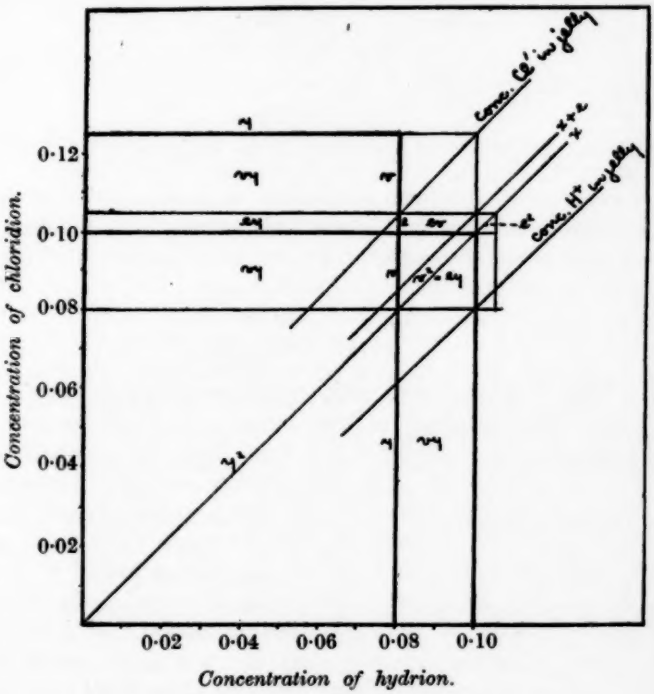
These relations can be represented graphically for any value of x, as is shown in Fig. 1.

Any one variable can be derived in terms of any other two, but in no case, from only the two equations given, can an equation be derived containing only two variables. As was pointed out previously, however, z was found from experiment to be equal approximately to $\sqrt{0{\cdot}02x+0{\cdot}0002}$, which bears a resemblance to one of the derived equations, namely, $z=\sqrt{4ex+e^2}$. Putting $e=0{\cdot}005$, we get $z=\sqrt{0{\cdot}02x+0{\cdot}000025}$, which is strikingly like the one obtained empirically, but gives low values for concentrations less than $x=0{\cdot}03$. Theoretical considerations rendered it improbable that e, considered in the general way in which we have done, could be a real constant, but it is difficult to obtain a smooth experimental curve from the formula $e=\frac{(x-y)^2}{y}$, because small errors in y correspond with large errors in e, and it is not possible to determine y in the most dilute solutions with very great accuracy by volumetric methods.

It occurred to us, however, that if we could incorporate the volume of the jelly, which can be determined with great accuracy, into an equation containing only two other variables, it would at once be possible to calculate any variable from V and x only. It

was found that the theory could be summed up in the form of such an equation, which could readily be subjected to the rigid test of experiment. The notation used is that mentioned earlier in the paper. The degree of ionisation of any given electrolyte, MN, is often expressed by the formula $[M^+] \times [N'] = K[MN]$, where K may be nearly constant, as in the case of acetic acid, or a variable, as in the case of highly ionisable electrolytes. In the following,

FIG. 1.



$x = 0{\cdot}10$ $z = 0{\cdot}045$
$y = 0{\cdot}08$ $a = 0{\cdot}005$
$v = x - y.$

gelatin chloride is considered to be ionised into gelatin ion and chloridion, and the gelatin ion to be ionised still further into gelatin molecule and hydrion. A similar case would be the ionisation of ammonium chloride into ammonion, and chloridion and the further ionisation of the ammonion into ammonia and hydrion. We may therefore write:

(*a*) [gelatin ion] $\times$ [Cl'] $= K$[gelatin chloride] or $z(y+z) = Ka$.
(*b*) [gelatin molecule] $\times$ [H^+] $= K'$[gelatin ion] or $y(g-a-z) = K'z$.

By solving (*a*) and (*b*) simultaneously to remove the term in *a*:

$$(c)\quad Kgy = y^2z + Kyz + yz^2 + KK'z.$$

Taking Procter's figure of 839 for the molecular weight of a unit of gelatin, 1 gram of gelatin represents 0·00119 gram-equivalent. Therefore at any volume:

$$(d)\quad g = \frac{1{\cdot}19}{V}$$

Substituting (*d*) in (*c*) and simplifying:

$$(e)\quad V = \frac{1{\cdot}19Ky}{z(y^2 + Ky + yz + KK')}.$$

Or in terms of x and y:

$$(f)\quad V = \frac{1{\cdot}19Ky^2}{(x^2 - y^2)(x^2 + Ky + KK')}$$

The value of K' has been considered to be so small that neglecting it should produce no appreciable errors in concentrations greater than $x = 0{\cdot}005$, so that for these more concentrated solutions the equation reduces to:

$$(g)\quad V = \frac{1{\cdot}19Ky^2}{(x^2 - y^2)(x^2 + Ky)}.$$

Now K has been assumed, with good reason, to be nearly equal to the ionisation-constant of hydrochloric acid for corresponding concentrations. It will be noted from the above equation that small errors in the value of K will produce negligible errors in the calculations so long as the value of Ky is considerably greater than that of x^2, and such a condition does obtain in these more concentrated solutions so long as K is the ionisation-constant of a strong electrolyte. For the present set of calculations, then, it will be permissible to take K as the ionisation-constant of hydrochloric acid, which is known approximately for any given concentration. Moreover, since it has been shown that, in these more concentrated solutions, almost all the gelatin has been converted into the monochloride, we are justified in taking K as the ionisation-constant of hydrochloric acid at concentration g, where g is simply $\frac{1{\cdot}19}{V}$. Now from experimental values for V and x it is possible to calculate values for y, which should not differ from the value obtained from experiment by more than would be attributed to experimental error. The results are given in table I.

TABLE I.

Determined as noted above.*	By experiment.			Calculated.
K	V	x	y	y
0·95	16·9	0·262	0·228	0·237
0·94	17·5	0·220	0·186	0·195
0·88	20·2	0·174	0·145	0·152
0·85	21·6	0·153	0·123	0·132
0·85	21·6	0·130	0·105	0·108
0·83	22·4	0·108	0·080	0·087
0·80	24·1	0·087	0·066	0·068
0·75	25·9	0·064	0·049	0·047
0·65	34·3	0·0386	0·028	0·026
0·56	45·6	0·0165	0·0084	0·0084
0·55	49·4	0·0118	0·0057	0·0050
0·50	56·4	0·0071	0·0020	0·0022

* These calculations are based on the figures of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781) and those of Noyes and Falk (*ibid.*, 1912, **34**, 454).

The agreement between experimental and calculated values bears out the theory remarkably well, the differences being not greater than was to be expected, considering the difficulties in titrating small quantities of solutions containing traces of organic matter. We feel that values for e calculated from V and x by this formula will be approximately correct. Of course, it is evident that in the very dilute solutions K' ceases to be a negligible quantity. Preliminary experiments with the hydrogen electrode show that K' is of the order of 0·00015, which fully justifies our assumptions in neglecting it for the higher concentrations.

In Figs. 2 and 3 curves are given for the various variables as functions of x. The values for V, x, and y were obtained directly from experiment, whilst those of z and e were calculated by means of the above formula. It will be noted by reference to Figs. 2 and 3 that e apparently varies directly as the volume. Such a relation, if it could be proved, would simplify all other relations to the extent that any variable could be expressed, with suitable constants, in terms of any other one, and the theory, as such, might well be said to be complete.

It was conceived that by means of the hydrogen electrode we could determine all the variables in a special experiment in which the volume was kept more nearly constant. One gram of gelatin was dissolved in such a quantity of water that at 33° the volume was 21 c.c. This high temperature was used because it is necessary to make hydrion determinations in the melted jelly. The method of using the hydrogen electrode was similar to that used and described by Sörensen (*Compt. rend. lab. Carlsberg*, 1909, **8**, 59). Acid was added at intervals and the hydrion concentration

By solving (*a*) and (*b*) simultaneously to remove the term in a:

$$(c)\quad Kgy = y^2z + Kyz + yz^2 + KK'z.$$

Taking Procter's figure of 839 for the molecular weight of a unit of gelatin, 1 gram of gelatin represents 0·00119 gram-equivalent. Therefore at any volume:

$$(d)\quad g = \frac{1{\cdot}19}{V}$$

Substituting (*d*) in (*c*) and simplifying:

$$(e)\quad V = \frac{1{\cdot}19Ky}{z(y^2 + Ky + yz + KK')}.$$

Or in terms of x and y:

$$(f)\quad V = \frac{1{\cdot}19Ky^2}{(x^2 - y^2)(x^2 + Ky + KK')}$$

The value of K' has been considered to be so small that neglecting it should produce no appreciable errors in concentrations greater than $x = 0{\cdot}005$, so that for these more concentrated solutions the equation reduces to:

$$(g)\quad V = \frac{1{\cdot}19Ky^2}{(x^2 - y^2)(x^2 + Ky)}.$$

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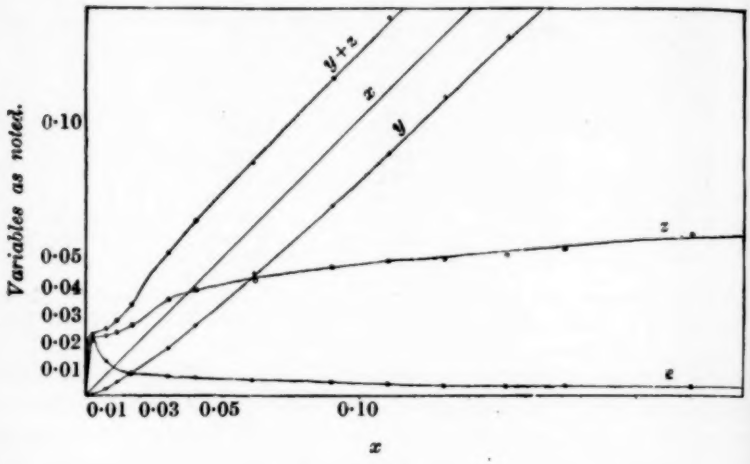
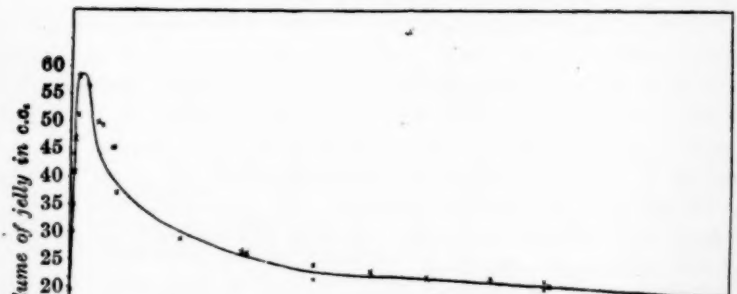
determined. From the figures obtained it was found possible to calculate all the variables desired. Knowing the quantity of

FIG. 2.



acid added, it was possible to calculate, from the hydrion concentration found, the amount which had combined with the gelatin, and consequently the total concentration of gelatin chloride, giving

FIG. 3.



values for y and $a+z$. Whilst actually there is no external solution, there is a theoretical one, since the products of hydrion and chlorid-

ion must be equal in both phases; that is, the product $y(y+z)$ of the jelly is equal to the x^2 of a theoretical external solution. If, as before, we regard the gelatin chloride as ionised to about the same extent as hydrochloric acid, we can take K as the ionisation-constant of hydrochloric acid at a concentration of $a+z$, which is known. From the equation $z(y+z)=Ka$ it follows that:

$$z=\frac{-(K+y)+\sqrt{(K+y)^2+4K(a+z)}}{2}$$

in which all terms on the right-hand side are known, and consequently z can be calculated. From y and z, also, all other variables can be calculated by formulæ presented earlier in the paper. The results obtained in this way are given in table II, and are shown graphically in Fig. 4.

TABLE II.

c.c. N/$_{10}$-HCl added.	Volume produced. V.	Concentration of acid produced.	Concentration hydrion found. y	Concentration of acid found.	Concentration acid combined. $a+z$	z	x	e	$y+z$
0·0	21·0	—	0·000003	—	—	—	—	—	—
0·1	21·1	0·002381	0·000006	0·000006	0·002375	0·002351	0·000119	0·002128	0·002357
0·2	21·2	0·004762	0·000011	0·000011	0·004751	0·004614	0·000226	0·004202	0·004625
0·3	21·3	0·007143	0·000016	0·000016	0·007127	0·006965	0·000334	0·006320	0·006981
0·4	21·4	0·009345	0·000030	0·000030	0·009315	0·009064	0·000522	0·008069	0·009094
0·5	21·5	0·011628	0·000046	0·000046	0·011582	0·011229	0·000718	0·009817	0·011275
0·6	21·6	0·013888	0·000048	0·000048	0·013840	0·013390	0·000803	0·011875	0·013438
0·8	21·8	0·018348	0·000117	0·000117	0·018231	0·017665	0·001442	0·015005	0·017782
1·0	22·0	0·022727	0·000246	0·000247	0·022480	0·021555	0·00232	0·01741	0·021801
1·4	22·4	0·031250	0·00100	0·00101	0·03024	0·02881	0·00559	0·02107	0·02981
2·0	23·0	0·043478	0·00501	0·00511	0·03837	0·03621	0·01437	0·01748	0·04122
3·0	24·0	0·062500	0·0193	0·0201	0·0424	0·03928	0·0336	0·01059	0·0586
4·0	25·0	0·080000	0·0335	0·0350	0·0450	0·04098	0·0500	0·00813	0·0745
5·0	26·0	0·096154	0·0492	0·0521	0·0440	0·03935	0·0660	0·00573	0·0886

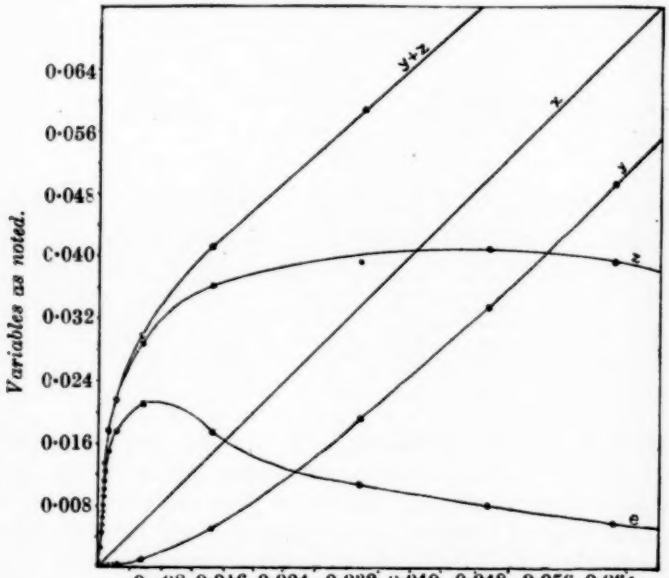
The curve of special interest is that of the variable e, which is seen to increase to a maximum at a very low concentration and then to fall in a manner similar to that of the volume curve (Fig. 2). Since e represents the measure of an outward pressure, we have, when the jelly is free to swell, an application of a special case of Hooke's Law, *ut tensio sic vis*, where stress $=c\times$ strain; and since e is a uniform pressure, it follows that it will produce an increase in the size of the jelly, but not in its shape, and that the increase in volume will be directly proportional to the pull. If we take the volume of 1 gram of dry gelatin as 0·7 c.c., then, so long as the elastic limit is not exceeded, $e=k(V-0{\cdot}7)$, where the value of the constant is determined by the bulk modulus of the gelatin or particular protein under consideration. The relation is therefore dependent on the temperature, and that this is an appreciable factor is shown by the following rough experiments:

Initial concentration of acid.	Volume of jelly		
	7°.	15°.	33°.
0·200	11·3	17·6	—
0·100	13·0	19·8	—
0·050	14·6	23·2	33·0*
0·025	18·5	27·3	—
0·010	22·2	34·3	—

* The value for the volume at 33°, a temperature well above the melting point of the jelly, is approximate only, and was obtained by gradually raising the temperature of the swollen jelly and its equilibrium acid, when the jelly, from its gravity and viscosity, does not mix with the supernatant liquid.

It is probable that the effect produced by this limited rise of temperature is not due to material changes in ionisation or chemical

FIG. 4.



activity, but almost solely to the diminution of the solid cohesion of the jelly. Many reasons convince us that the cohesive forces of the jelly opposing e are still maintained beyond the melting point.

It is evident that the volume of the jelly, at a constant temperature, is dependent for its value on the value of e, and the only remaining question is why the value of e should follow a curve of the particular type that it does. As was noted earlier in the paper,

the following equation results from a simultaneous solution of the thermodynamic and osmotic equations given:

$$e = -2x + \sqrt{4x^2 + z^2}.$$

As the concentration of acid is increased from zero to some small, but finite, value, z must necessarily increase at a very much greater rate than x. This is shown very markedly in the most dilute solutions, where almost all the acid added combines with the gelatin: but z has a limiting value, which is determined by the total concentration of gelatin with which we started. Now z must either approach this limiting value or diminish, which it would do if the ionisation of the gelatin chloride were sufficiently repressed. In either case:

$$\lim_{x=\infty} \sqrt{4x^2 - z^2} = \sqrt{4x^2},$$

from which it follows that:

$$\lim_{x=\infty} e = -2x + 2x = 0.$$

It is clear from this that, as x increases from zero, e must increase to a maximum and then decrease, approaching zero asymptotically, regardless of whether or not the ionisation of the gelatin salt is appreciably repressed. In Fig. 4 it will be seen that e begins to decrease at a considerable rate while z is still increasing slightly, which would be expected. It should be noted that the apparent decrease in z in the most concentrated solution, given in table II, is due chiefly to the increased volume.

An interesting point is raised here regarding the action of salt in repressing the swelling of jelly swollen with acid. Whilst the salt undoubtedly represses the ionisation of the gelatin chloride to some extent, it would scarcely be sufficient to account for the fact that salt reduces the volume of jelly almost to that of dry gelatin. The chief action is probably that the addition of salt corresponds with an increase in the value of x, and that this increase in x must, according to the equation just discussed, produce a decrease in the value of e, with a corresponding diminution of the volume of the jelly.

Summary.

When gelatin is immersed in a dilute solution of an acid, combination takes place between the gelatin molecules and the hydrogen ions, resulting in the formation of a highly ionisable salt of gelatin, the anion of which in tending to diffuse exerts on the jelly mass an outward pull, which, being uniform in all directions, produces, according to Hooke's Law, an increase in the volume of the jelly proportional to the magnitude of the pull. In the case of gelatin

immersed in a very dilute solution of a highly ionisable acid (say, 1 gram of gelatin in 100 c.c. of $N/1000$-hydrochloric acid) almost all the acid combines with the gelatin, and we have the simplest type of equilibrium, where, practically, $x=0$, $y=0$, $y+z=z=e$, and the concentration of the anion of the jelly is the measure of the outward pull and consequently of the increase in volume. In more concentrated acid solution (say, 1 gram of gelatin in 100 c.c. of $N/10$-hydrochloric acid) only a part of the acid combines with the jelly, and we have $y+z>z>e$, but here it is neither the total concentration of anion of the jelly nor that of the ionised gelatin salt which is the measure of the force producing swelling, but it is the excess of concentration of diffusible ions of the jelly over that of the external solution. This quantity e is a direct measure of the swelling so long as the swelling does not exceed the elastic limit, and offers a complete explanation of the peculiar swelling curve obtained by immersing gelatin in increasing concentrations of hydrochloric acid (see Fig. 2). In the most dilute solutions e will increase almost directly with the increasing initial concentration of acid, but will approach a maximum as the formation of the gelatin monochloride nears completion, and must then decrease as x becomes larger, according to the equation $e=-2x+\sqrt{4x^2+z^2}$, where z has a limiting maximum value. The repression of swelling by the addition of salt is caused by the apparent increase in the value of x produced, which results in a diminution of the value of e and consequently in a repression of the swelling, this action being assisted to some extent by the repression of the ionisation of the gelatin salt.

In the case of weak acids, like acetic, a greater total concentration of the acid is required to produce nearly complete combination of the gelatin with the acid, because the degree of combination is determined by the value of y, which, even in the more concentrated solutions, will be small because of the repression of the ionisation of the acid by the highly ionisable gelatin salt. For this reason the swelling of gelatin in acetic acid increases with increasing total concentration of acid, and is not repressed by the addition of an excess; in fact, the swelling continues up to a strength of acid of $N/1$ beyond which solution of the gelatin takes place. The somewhat stronger formic acid actually shows slight repression, whilst very weak acids, such as boric, as would be expected, produce little, if any, swelling.

In pure water, combination must take place, although probably only to a very slight extent, between the gelatin molecules and the hydrion of the slightly dissociated water, leaving in the jelly a corresponding excess of hydroxyl ions which tend to diffuse out-

ward, causing the jelly to swell. The presence of sulphites in the gelatin and carbonic acid in the water tend, of course, to produce a greater swelling than the minimum, which would result from pure gelatin and water, difficult, if possible, to obtain.

Some work has been done on the equilibrium of gelatin and alkalis, but solution of the gelatin took place at so low a concentration of the alkali (at about $x=0{\cdot}04$ for sodium hydroxide at 20°) that the work could not be carried out to the extent desired. Work on hide has shown that the swelling is repressed either by the addition of excess of alkali or by the addition of ammonium chloride. In the former case the swelling is repressed by the increase in the value of x, according to the law derived for acids; in the latter case by bringing the solution back almost to a condition of neutrality, the gelatin compound being again decomposed. It is probable that the laws governing alkaline-swelling are the same as those governing acid-swelling.

It will be seen that the laws discussed are quite general, and that for any particular sample of gelatin at constant temperature any variable can be expressed as a direct function of x, and that for all acids the value of K' will be the same, whilst the value of K is merely dependent on the degree of ionisation of the gelatin salt formed. With suitable values for K, K', and k, the laws are probably applicable to any protein and any acid or alkali.

If, as the authors believe, the foregoing theory is not merely applicable to gelatin, but, with appropriate constants to the colloidal swelling of all proteins, it is obviously of far-reaching importance, not merely to the special technology in which it originated, but to many physiological and medical problems. It is only necessary to allude to the work of Loeb on the fertilisation of the *Echinus* egg by saline solutions, of Fischer on œdema, and of Pauli and others who attribute muscular energy to colloidal swelling and contraction produced by the alternate action of sarcolactic acid and the saline constituents of the blood; whilst many of the problems of plant-growth and of the semipermeability of vegetable membranes are probably due to analogous causes; and the laws which regulate the swelling of carbohydrate jellies, such as agar-agar, starch, and cellulose itself demand a similar investigation.

PROCTER INTERNATIONAL RESEARCH LABORATORY,
UNIVERSITY OF LEEDS. [*Received, February 18th*, 1916].

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 30TH, 1916, AT 4 P.M.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President, in the Chair.

Dr. DAVID HOOPER and Dr. F. CHALLENGER were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT announced that the Council had received two munificent donations to the Research Fund of the Society: £1,000 from Dr. G. B. Longstaff, whose father, by a gift of a similar amount, was largely instrumental in founding the Research Fund forty years ago, and £1,000 from Mrs. and Miss Müller, in commemoration of the late Dr. Hugo Müller's long connexion with the Society.

The Report of the Council on the progress of the Society during the last year was presented by the President, and a statement as to the income and expenditure for 1915 was made by the Treasurer, who also announced that the Council had received a further gift of £500 to the Research Fund from Dr. Alexander Scott, to mark his appreciation of the valuable work done by the Research Fund and in commemoration of the seventy-fifth Anniversary of the Society.

The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31st, 1915, was proposed by Professor W. J. POPE and seconded by Professor A. HARDEN. Speaking to this motion, Mr. JOHN HUGHES suggested that research grants should be made only for research carried out and subsequently published in the *Journal* of the Society. The President replied that the matter should receive the careful attention of the Council.

REPORT OF COUNCIL, 1915—1916.

On December 31st, 1914, the number of Fellows was 3,205. During 1915, 99 Fellows were elected and 9 were reinstated, making a gross total of 3,313. The Society has to mourn the loss of

44 Fellows by death; 35 Fellows have resigned, the elections of 2 Fellows have become void, and 29 Fellows have been removed for non-payment of annual subscriptions. The total number of Fellows, therefore, on December 31st, 1915, was 3,203, showing a decrease of two in comparison with the number of Fellows at the same date in the preceding year.

Since the last Anniversary meeting, the Council has suffered the loss of three Past-Presidents:

	President.	Died.
Raphael Meldola (1871)	1905–07	Nov. 16th, 1915.
Hugo Müller (1854)	1885–87	May 23rd, 1915.
Henry Enfield Roscoe (1855)	1880–82	Dec. 18th, 1915.

The Council desires to record that the following seven Fellows have fallen in action:

Charles Maurice Berlein (1913).
John Llewelyn Davies (1905).
James Louis Foucar (1906).
Ivan Richard Gibbs (1914).
Richard Arnold Seymour-Jones (1912).
Frank Stevenson Long (1910).
Benjamin Ashwell Posford (1910).

Obituary notices of these Fellows will appear in the Transactions during the present year.

The names of the other deceased Fellows, with the dates of election, are:

John Henry Baldock (1873).
Alec Alfred Beadle (1897).
John Jacob Beringer (1882).
Richard Berncastle (1890).
Nathaniel Bradley (1876).
Frank Buckley (1915).
Robert John Caldwell (1904).
Robert Carruthers (1882).
Arthur Herbert Church (1856).
Henry Crookes (1902).
William Drake Crumbie (1884).
Heinrich Debus (1859).
George Price Dodds (1892).
Henry Durham (1871).
John Gill (1888).
Edward Gillman (1901).
Tamemasa Haga (1886).
Christopher Hodgson (1886).
Edmund Foster Hudson (1900).
Frank Jagger (1915).
Arthur Sheridan Lea (1890).
Vivian Byam Lewes (1888).
David Alexander Louis (1878).
John George Lyon (1874).
Francis Henry Neville (1890).
Andrew Noble (1869).
John O'Sullivan (1899).
Thomas Law Patterson (1870).
Frederick Ernest Pollard (1888).
James Holms Pollok (1894).
Sidney George Rawson (1884).
William James Sell (1892).
John Walter Smith (1913).
Otto Nikolaus Witt (1876).

The following Fellows have resigned:

Arthur James Child.
Martin Dechan.
Edwin Mortimer Eagles.
Edgar Leeder Edlin.
Ralph Roscoe Enfield.
William Hall.
James Ballantyne Hannay.
Herbert Harding.
Robert Main Harland.
Sidney Harvey.
Thomas Holgate.
Henry Jackson.
Harold Bramfield Jones.
Leonard Gibbes Killby.

James Knight.
Brian Piers Lascelles.
Charles Pask Matthews.
Alfred Nixon.
Alexander Orr.
George Patterson.
Ernest Vivian Pearce.
Robert James Porter.
Clifford Clare Rattey.
Albert Sasson.
Ernest George Scott.
George Stone.
Frank Tutin.
Cuthbert Vaux.
Herbert Horace Ward.
James Whittle.
Charles Wightman.
Thomas Rowland Wingfield.
Percy James Winser.
John Middleton Wyborn.
Israel Hyman Zortman.

The number of Honorary and Foreign Members at the end of 1914 was 32. Since then the Society has lost Dr. Hugo Schiff, who died in Florence on September 8th, 1915. The total number of Honorary and Foreign Members at the end of 1915, therefore, was 31.

The following have been elected Fellows during 1915:

	Elected.
Basil Albert Adams	December 2nd
Frank Theodore Alpe	May 6th
Alfred Anderson	December 2nd
William Archibald Andrews	December 2nd
Frederick Louis Armitage	June 17th
Frederic Sutcliffe Aumonier	December 2nd
Alfred Louis Bacharach	May 6th
Frederick Charles Ball	May 6th
Thomas Hedley Barry	December 2nd
John Lloyd Bentley	May 6th
Samuel Culloch Bone	February 18th
Sidney Albert Brazier	February 18th
Neal Brodie	February 18th
William Alfred Bromwich	June 17th
Frank Buckley	February 18th
William Arthur Bush	December 2nd
Joseph Herbert Canning	December 2nd
Manmatha Nath Chatterji	February 18th
Pinzen Cheng	June 17th
George Roger Clemo	June 17th
Owen Colverd	December 2nd
Sydney Francis William Crundall	December 2nd
Premananda Das	May 6th
David Owen Davies	June 17th
Walter Thomas Davies	February 18th
Bhaskar Balvant Dhavale	December 2nd
John Gerald Frederick Druce	February 18th
Pavitra Kumar Dutt	December 2nd
Reginald Ernest Essery	May 6th
Henry Jackson Evans	May 6th
Robert George Fargher	February 18th
Robert Edward Forbester	May 6th
James Fraser	February 18th

	Elected.
Nagardas Purushottam Gandhi...	February 18th
Sudhamoy Ghosh	December 2nd
Charles Stanley Graham	December 2nd
Harri Heap	May 6th
Albert Richard Henchley	June 17th
Charles Hinde	May 6th
Ernest James Hoy	December 2nd
George Stanley Irving	December 2nd
Frank Jagger	June 17th
Lemuel Lucas Joshi	February 18th
James Kendall	December 2nd
Joseph Charles Kernot	December 2nd
William Kitto	December 2nd
Nikolai Semenovitsch Kurnakov	May 6th
John William Lee.....	December 2nd
Colin Henry Lumsden	May 6th
Thomas Morison Maben.....	February 18th
Ronald MacInnes	February 18th
Thomas McLachlan	December 2nd
Sreenagula Mallannah	February 18th
Kenneth George Marsden	February 18th
Frederick Alfred Mason	February 18th
John Ernest Mason	May 6th
John Livingston Michie	December 2nd
John William Mitchley	February 18th
Thomas Dagomet Morson	May 6th
Oswald James Walter Napier.....	December 2nd
Elton Arthur Nash	December 2nd
Archibald Durrant Ollé	December 2nd
Reginald Robert Outram	February 18th
Albert Parker	February 18th
Frank Peachey	June 17th
Archibald Ramsden Pearson	December 2nd
Arnaldo Piutti	December 2nd
Wilfrid Gustav Polack.....	December 2nd
James Walker Porter	December 2nd
Alfred Potter	December 2nd
Kodlapur Bhima Rau	December 2nd
Henry Taylor Fowkes Rhodes ...	May 6th
George Scott Robertson.....	December 2nd
Arthur Dawes Robinson	February 18th
Fred Robinson	December 2nd
David Charles Roberts	May 6th
Charles Smart Roy	February 18th
Harold Gordon Rule.....	February 18th
Nuggehally Sampataiengar	December 2nd
Godfrey Edward Scharff	December 2nd
Ramtaran Sen	February 18th
John Sewell	December 2nd
Harry Shulman	February 18th
Sydney Smith	February 18th
Vincent Harold Smith.....	December 2nd

	Elected.
John Taylor	February 18th
Henry Terrey	February 18th
Hugh Wolseley Thomas	December 2nd
Henry Burroughs Tilden	December 2nd
Su-Hian Ting	February 18th
Warwick Oben Gurney Trehair	December 2nd
Walter Ratledge Twigg	June 17th
Mohammad Sana Ullah	December 2nd
Harry Maas Ullmann	December 2nd
Kadayam Chudamani Viraraghavan	December 2nd
George Walworth	December 2nd
Leonard Richmond Wheeler	May 6th
Maurice White	February 18th
Willis John Williams	December 2nd

The hearty congratulations of the Council are offered to Professor George Carey Foster (elected March 3rd, 1856), who has been sixty years a Fellow, and to the following, who have attained their jubilee as Fellows:

Arthur Clegg Bowdler (elected April 20th, 1865).
Thomas Fairley (elected May 18th, 1865).
Sir William Augustus Tilden (elected June 1st, 1865).
James Parkinson (elected November 2nd, 1865).
Charles Umney (elected November 16th, 1865).
William Edward Bickerdike (elected December 7th, 1865).
Sir Boverton Redwood, Bart. (elected January 18th, 1866).

The volume of Transactions for 1915 contains 1,862 pages, of which 1,770 are occupied by 200 memoirs, the remaining 92 pages being devoted to the Obituary Notices, the first of the new lectures on special subjects, the account of the deputations of the Royal Society and the Chemical Society to the Government on the Position of Chemical Industries, the report of the International Committee on Atomic Weights, the report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contained 272 memoirs, occupying 2,830 pages. The Journal for 1915 also contains 4,223 abstracts, occupying 1,944 pages, whilst the abstracts for 1914 numbered 4,757 and occupied 2,068 pages. These figures do not truly represent the relative output of chemical papers in the two years. It was mentioned in the last Report that many of the Continental journals had not been available for abstraction since the commencement of the war. In the spring of 1915 most of these journals were obtained, and abstracts of the papers in them will be found in the volume for 1915, which therefore contains a considerable number of abstracts that should have appeared in

that of 1914. Since then most of the Continental journals have been obtained with moderate regularity, although of necessity there is some delay in their arrival.

The abstracts may be classified as follows:

PART I.

	Pages.	No of Abstracts.
Organic Chemistry		1,387
Physiological Chemistry		541
Chemistry of Vegetable Physiology and Agriculture		287
	1,092	2,215

PART II.

General and Physical Chemistry		889
Inorganic Chemistry		364
Mineralogical Chemistry		103
Analytical Chemistry		652
	852	2,008
Total in Parts I. and II.	1,944	4,223

At the request of the Board of Education it was decided to send a complete set of the Annual Reports and the Journal for 1915 and onwards for the use of the civil prisoners of war interned at Ruhleben, near Berlin.

The Council has postponed for a year the Annual Report on Radioactivity, and will publish in Vol. XIII. a Report dealing with the progress made in this subject during the years 1915 and 1916.

A year ago mention was made that the Council had under consideration the question of the occasional delivery of lectures on subjects of special interest. Arrangements have since been made for three lectures to be given during the Session 1915–1916. The first of these lectures was delivered on November 18th by Dr. E. J. Russell, who chose as his subject, "The Principles of Crop Production." This lecture has been published in the Transactions for 1915. The second lecture, entitled, "The Recent Work on *X*-Rays and Crystals, and its Bearing on Chemistry," was delivered by Professor W. H. Bragg on February 3rd, 1916, and will appear in the Transactions for March of the current year. The third lecture, entitled, "Newer Standpoints in the Chemical Study of Nutrition," will be given on May 18th by Professor F. Gowland Hopkins.

The Council is gratified by the large attendance at the lectures and by the continued interest shown by Fellows in the three informal meetings held during the past year. Owing to the abnormal circumstances at the present time, the Ordinary Scientific Meetings now begin at 8 o'clock instead of 8.30 p.m.

Last year Prof. W. H. Perkin delivered his Presidential Address entitled, "The Position of the Organic Chemical Industry." On account of the national importance of this subject the Council decided that the Address should be widely distributed among men of public authority throughout the United Kingdom. Copies of the Address were accordingly sent to Members of the Houses of Parliament and to various educational and civic authorities. The Council is gratified to report that they have received many letters expressing keen appreciation of the value of the Address.

In response to an invitation received from the British Academy, the President and Professor J. M. Thomson were appointed to represent the Society on the National Committee for the reconstitution of the Library of Louvain University.

During the past year the Council has had under consideration many questions arising out of the state of war. In March, the Councils of the Royal Society and the Chemical Society each presented to the Government Memorials on the Position of the Chemical Industries, and asked the Prime Minister to receive their deputations. On May 6th, the President of the Board of Trade (the Rt. Hon. Walter Runciman, M.P.) and the President of the Board of Education (the Rt. Hon. J. A. Pease, M.P.) received the representatives of the two Societies. An abstract of the proceedings, together with copies of the memorials, appeared in the Transactions.

In June last, with the object of continuing their work without interruption during the vacation, the Council, by a special resolution, constituted itself a Consultative Body on all chemical matters arising out of the war. The President then addressed a letter to every Fellow, inviting him to forward to the Council any suggestions and inventions he might have to make, and also asking him to indicate on a form provided for the purpose the services he could best render to the country. A gratifying response has been received to this appeal; many suggestions and inventions have been forwarded by Fellows and by the public, and numerous offers of assistance have been received from Fellows in every part of the Empire. These offers of assistance have been tabulated, and a careful record has been forwarded to the Royal Society for future use.

In order to carry out effectively the work of considering the sug-

gestions received, the Council invited the co-operation of the following kindred Societies:

Royal Agricultural Society,
Biochemical Society,
Society of Chemical Industry,
Society of Dyers and Colourists,
Faraday Society,
Institute of Chemistry,
Institute of Metals,
Institute of Mining and Metallurgy,
Pharmaceutical Society,
Physical Society,
Society of Public Analysts.

The Council proposed that Special Committees should be appointed in order to examine and report on the suggestions and inventions submitted to them by the Council, and, thanks to the loyal and ready assistance extended by these Societies, ten Committees were formed and have been carrying out the duties entrusted to them. Each Committee consists of eight members, six of whom are appointed by the co-operating Society and two by the Chemical Society, thus forming a direct link between the Committee and the Council. The Committees have reported to the Council the results of their deliberations; those suggestions considered suitable were then sent on to the proper Government authorities, who have expressed their high appreciation of the valuable assistance thus afforded them. The Society has also been instrumental in aiding the Ministry of Munitions with regard to the supply of chemists for the manufacture of munitions of war.

In addition to these Special Committees, which deal chiefly with matters of practical detail and utility, a General Committee has been formed consisting of two members elected by each of the co-operating Societies. The object of this General Committee is to consider and discuss all questions of general policy, not only those arising from the war, but those matters on which it is desirable to have the opinion of a body thoroughly representative of every department of chemical science.

The Council has also taken action in connection with the Government scheme for the organisation and development of scientific and industrial research under the auspices of the Board of Education. The President addressed an appeal to Fellows inviting them to forward to the Society suggestions for suitable researches, bearing more especially on the chemical and allied industries. Many valuable suggestions have already been received, and after the careful consideration of the Council a selected number have been forwarded to the Advisory Council for Scientific and Industrial Research.

Since many important questions concerning the relations of chemical science to industry were found to be involved in the development of this scheme, the Council invited the Councils of the

Society of Chemical Industry and of the Society of Dyers and Colourists to meet them at a conference on November 4th to consider the best methods for promoting co-operation amongst chemical manufacturers and between them and the teachers in universities, colleges, and technical schools. So many questions were raised at this meeting that it was decided to request the Council of the Society of Chemical Industry to appoint a committee of nine members to draw up a scheme for consideration by the three Councils. The report of this Committee was received at a meeting held on March 6th; it was then resolved "that it is desirable that an association of firms engaged in chemical manufacture and its allied industries be formed." Steps are now being taken to carry this resolution into effect.

A request has been received from the Board of Agriculture and Fisheries that the Society should arrange for the preparation of a report concerning the different processes of manufacture of nitrates and ammonium salts, indicating their respective merits from the standpoint of British conditions. The Council have acceded to the request, and have appointed Lt.-Col. Arthur W. Crossley, Professor Threlfall, and Mr. G. S. Albright to prepare the report.

The number of books borrowed from the Library during the year 1915 was 1,541, as against 1,922 the previous year; of these 446 were issued by post, as against 668 in the preceding year.

The additions to the Library comprise: 90 books, of which 46 were presented, 349 volumes of periodicals and 29 pamphlets, as against 95 books, 265 volumes of periodicals, and 45 pamphlets last year.

A further removal to the basement store of some 500 volumes of books but seldom used has permitted several improvements in the general arrangement of the Society's Library, of which the following may be mentioned:—

(i) A further collection of early editions and works of historical interest has been placed in the glazed case by the side of that containing the alchemical books.

(ii) The section of history and biography has been removed to its natural position near to the above-mentioned volumes.

(iii) The removal of the latter books has made room for the extension of the section of applied chemistry.

These alterations have necessitated the compilation of a new Shelf Register.

In consequence of inquiries which have been made from time to time by Fellows regarding portraits of early chemists for purposes of identification, illustration of lectures, etc., the portraits

of chemists in books in the Library other than periodicals have been card indexed. This index already contains 650 entries.

Passing now to the annual review of the Society's finances, the Council has gratification in announcing a balance of income over expenditure amounting to £821 13*s.* 9*d.* At the time of making the previous statement it was not possible to estimate the effect of the war, for although the immediate result had been to reduce expenditure on the Journal, it was reasonable to entertain forebodings in respect of increased outlay for unusual purposes, accompanied by reduction in admission fees and subscriptions. Happily the last-named causes have not operated to the extent which might have been anticipated, as admission fees amounted to £356, instead of £564 in 1914, whilst the loss in subscriptions is represented by the difference between £5,103 and £4,995; the total reduction from these two sources, therefore, amounts only to £316, and is diminished by an increase of £33 in life composition fees. Moreover, the reduction in dividends, £28 17*s.* 9*d.*, is more apparent than real, a portion of this being recoverable, whilst the sale of publications account shows an increase of £37 15*s.* 7*d.*, owing to the prudent policy of raising the price of the Journal from £2 to £3 per annum, announced in the last Report; this has brought in £274 3*s.* 6*d.* more than last year from sale of Journals, whilst Collective Index sales have fallen from £213 1*s.* 11*d.* to £44 11*s.* 4*d.* On the other hand, the proceeds from advertisements have diminished by £75 19*s.* 5*d.*, for the very simple reason that in these days chemical products dispose of themselves more rapidly than they can be manufactured. With a small windfall of £54 12*s.* 3*d.* arising from a revision of printing charges during the past eleven years, the total diminution of income is only a few shillings over £300.

The excess of income over expenditure comes mainly from a diminished Journal and a change of form in the Proceedings, the charges on these accounts having fallen from £5,833 6*s.* 8*d.* to £4,674 16*s.* 7*d.* In this connexion the following figures, bringing the years 1913, 1914, and 1915 into review, will explain the position and indicate the effect of the war on the Transactions and Abstracts respectively:

	1913. Number of pages.		1914. Number of pages.		1915. Number of pages.	
	Trans.	Abs.	Trans.	Abs.	Trans.	Abs.
Jan.–June ...	1266	1228	1696	1300	918	876
July–Dec. ...	1030	1292	1213	768	944	1068
Totals	2296 + 2520		2909 + 2068		1862 + 1944	
	4816		4977		3806	

The reduction in Abstracts during the latter half of 1914 is due to the diminished number of foreign journals reaching the country; these began to arrive in attenuated form during the early part of 1915, so that the total for the full war-year approximates to that in 1914, although smaller than that of 1913 by 576 pages. It is in the Transactions, however, that the greatest diminution occurs. Comparing the first six months of 1913, 1914, and 1915, the page-totals are 1,266, 1,696, and 918 respectively, and the reduction in output of original work by our Fellows for the whole period of 1915 compared with 1914 is represented by the difference between 2,909 and 1,862 pages; it is proper to point out, however, that this is solely due to the diversion of their thoughts and energies into channels more immediately useful to the service of our country.

An increase of £190 15*s.* 10*d.* in administrative expense arises from several causes connected with the war. At the close of the year the Council felt justified in awarding a bonus to the staff in view of the serious increase in cost of commodities and in recognition of their cheerful co-operation in dealing with considerable extra labour entailed by the committee work which the Society has undertaken; in addition to these grants one-half the salary of Mr. H. J. Morris is being paid to him during his military service. It has been considered advisable to insure the Society's property against damage by hostile aircraft, and the outlay on office printing, stationery, and postage has increased by £85 11*s.* 3*d.* on account of the liberal postal intercourse which has been maintained between the Council and Fellows throughout the year. A hot-water system has been installed at an expenditure of about £30, but, on the other hand, an item of capital outlay mentioned in the previous Report has been the source of considerable saving; by means of the addressograph, the charge for wrappers and addressing, which amounted to £117 10*s.* 7*d.* in 1913, stands at only £3 2*s.* 7*d.* in the present account, so that this investment yields a handsome return.

As might be expected from existing circumstances, the Research Fund account reveals diminished activity in purely scientific work, and accordingly shows a balance on income over expenditure amounting to £297 13*s.* 6*d.* This is composed principally of £131 14*s.* 1*d.*, which has been returned by recipients of previous years, and the difference between the 1914 grants (£287) and those made in 1915 (£137). Although this large balance is not a matter for satisfaction, the Council hopes that the £300 of Exchequer Bonds which it has been thereby enabled to purchase on this account will render useful assistance to the research activity of happier years.

Liabilities.

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1915.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance				193	10	0
,, Sundry Creditors				915	5	2
,, Research Fund :—						
As per last Balance Sheet	10625	10	7			
Add Excess of Income over Expenditure for the year	297	13	6			
				10923	4	1
,, Chemical Society : Excess of Assets over Liabilities :—						
As per last Balance Sheet...	20418	4	0			
Add Excess of Income over Expenditure for the year	821	13	9			
				21239	17	9
				£33271	17	0

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1050 London and North Western Railway 3 per cent. Debenture Stock	889	12	0			
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460	13	6			
£1200 North British Railway 3 per cent. Debenture Stock	1033	11	0			
£700 Canada 2½ per cent. Stock, 1930/50	704	8	6			
(Estimated present value of Investments, £16879 2*s.* 9*d.*)				21001	19	11
,, Sundry Debtors :—	£	s.	d.			
Advertising Account	44	18	6			
Less Commission accrued	4	9	7			
				40	8	11
Other Societies				20	9	6
Messrs. Gurney & Jackson				726	15	5
Telephone Deposit				1	0	0
				788	13	10
,, Subscriptions in Arrear, £788. Estimated to realise ...				430	0	0
,, Insurance paid in advance				15	8	6
,, Cash at Bank				110	2	9
,, Cash in hand				2	7	11
,, Research Fund :—				112	10	8
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock				1010	0	0
£4400 Metropolitan Consolidated 3½ per cent. Stock				4587	18	0
£1034 Great Western Railway 2½ per cent. Debenture Stock				1049	15	11
£1142 16*s.* New South Wales 3 per cent. Stock ...				1000	0	0
£1122 Metropolitan Water Board 3 per cent. "B" Stock				1002	16	9
£1365 Midland Railway 2½ per cent. Debenture Stock				1010	0	9
£806 Victoria 3 per cent. Stock				706	6	2
(Estimated present value of Research Fund Investments. £8878 8*s.* 2*d.*)				10366	17	7
,, Cash at Bank...				556	6	6
				10923	4	1
				£33271	17	0

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions				190	0	0
,, Admission Fees				356	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1915	186	0	0			
,, during 1915 ,, ,,	4319	0	0			
,, ,, ,, ,, 1914	356	0	0			
,, ,, ,, ,, 1913 and previous	18	0	0			
	4879	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	320	0	0			
	4559	0	0			
Add Arrears at date: 1915, £734; 1914 and previous, £54, estimated to realise as per Balance Sheet	430	0	0			
				4989	0	0
,, Lady Subscribers				6	0	0
Investments:—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock	208	11	4			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock	28	7	7			
,, £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	40	9	11			
,, £1400 India 2½ per cent. Stock	31	0	0			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	49	12	6			
,, £4341 Midland Railway 2½ per cent. Preference Stock	97	4	5			
,, £1200 Leeds Corporation 3 per cent. Stock	31	19	0			
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	38	5	0			
,, £1200 North British Railway 3 per cent. Debenture Stock	31	1	9			
,, £700 Canada 3½ per cent. Stock 1930/50	21	13	11			
,, Income Tax Recovered	36	19	4			
,, Interest on Deposit Account	20	13	2			
				635	17	11
,, Publication Sales:—						
Journals	1377	16	0			
Proceedings	3	18	4			
Collective Index	44	11	4			
Memorial Lectures	6	2	6			
Library Catalogue		12	9			
Atomic Weight Tables		4	8			
Jubilee Volume		12	6			
Annual Reports on Progress of Chemistry	159	5	0			
	1593	3	1			
Less Publishers' Commission	154	7	5			
				1438	15	8
,, Proceeds of Advertisements in Journal	£128	5	0			
Less Commission	9	9	4			
				118	15	8
,, Miscellaneous Receipts				3	11	5
,, ,, ,, allowances on Printing Accounts in previous years				54	12	3
,, Subscriptions from other Societies				28	17	6
				£7821	10	5

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

23, QUEEN VICTORIA STREET, E.C.
March 2nd, 1916.

W. B KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1915.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal and Proceedings:—		
Salary of Editor, including Indexing	620 0 0	
Salary of Sub-Editor and Assistance	250 0 0	
Editorial Postages	24 13 3	
Abstractors' Fees	459 18 8	
Printing of Journal	2553 5 4	
Banding	* 41 4 10	
Printing of Advertisements	40 14 0	
Wrappers and Addressing	3 2 7	
Distribution of Journal	499 6 8	
Authors' Copies	141 2 9	
Insurance of Stock	5 3 9	
Printing of Proceedings Index, 1914	36 5 2	
		4674 16 7
„ Annual Reports on the Progress of Chemistry		405 10 9
„ Purchase of back numbers of Journal		7 17 9
„ List of Fellows		73 6 7
„ Library Expenses:—		
Salary of Librarian and Assistant	231 0 0	
Books and Periodicals	187 18 8	
Binding	64 0 10	
		482 19 6
„ Indexing for International Catalogue		30 0 0
„ Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological		10 0 0
„ Administrative Expenses:—		
Salary of Staff	347 12 0	
War Bonuses and Honorarium	98 5 0	
Wages (Commissionaire, Housekeeper, and Charwoman)	171 11 0	
Coal and Lighting	50 7 1	
House Expenses and Repairs	92 6 2	
Furniture	14 19 5	
Tea Expenses	44 4 9	
Insurances	27 3 1	
Accountants' Charges	21 0 0	
Commission on Recovery of Income Tax	1 16 9	
Law Costs	4 4 0	
Printing	134 7 8	
Stationery	92 6 4	
Postages	139 15 9	
Miscellaneous Expenses	35 6 6	
		1315 5 6
„ Balance, being excess of Income over Expenditure carried to Balance Sheet		821 13 9

* Including War bonus of £21 14s.

£7821 10 5

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—ALEXANDER PEDLE
A. LIVERSIDGE
CHARLES A. KEANE

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1915

Income.

	£	s.	d.	£	s.	d.
To Dividends on:—						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	36	1	5			
£4400 Metropolitan Consolidated 3½ per cent. Stock	136	7	2			
£1034 Great Western Railway 2½ per cent. Debenture Stock	23	5	10			
£1142 16s. New South Wales 3 per cent. Stock	30	7	2			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	30	0	4			
£1365 Midland Railway 2½ per cent. Debenture Stock	30	15	8			
£806 Victoria 3 per cent. Stock	21	8	2			
				308	5	9
Repayments of Research Grants:—						
T. E. Hull	12	10	0			
P. May	4	10	9			
C. F. Hawkins	5	0	0			
R. R. Baxter	7	0	0			
G. H. J. Adlam	1	16	10			
J. A. N. Friend		10	1			
W. H. Patterson		11	4			
J. C. Duff	1	3	3			
J. W. McBain	2	8	4			
W. C. Ball	3	2	2			
A. C. Dunningham	2	16	6			
Miss Marion Jones	1	14	0			
J. Kenner	7	0	0			
H. McCombie	1	0	0			
G. Blackstock	6	5	6			
G. W. Clough	1	12	8			
Brought forward—	59	1	5			
A. Forster	5	0	0			
W. H. Gibson	5	0	0			
W. J. Jones	5	0	0			
G. Martin	5	0	0			
F.M.G Micklethwait	3	4	8			
E. E. Turner	6	0	0			
C. H. Desch	1	8	0			
R. W. L. Clarke	1	16	9			
W. R. Pratt		16	2			
G. Barger	3	17	8			
F. Barrow	5	0	0			
D. Segaller	7	6	3			
J. L. Simonsen	13	0	10			
Miss M. S. Leslie	10	0	0			
R. Robinson		2	4			
				131	14	1
Carried forward— £59 1 5						
,, Income Tax Recovered				21	0	6
				£461	0	4

Expenditure.

	£	s.	d.	£	s.	d.
By Grants to—						
J. A. N. Friend	5	0	0			
B. N. Ghosh	10	0	0			
A. T. King	5	0	0			
F. A. Mason	10	0	0			
G. T. Morgan	10	0	0			
J. E. Purvis	20	0	0			
H. K. Sen-Gupta	12	0	0			
H. M. Spiers	15	0	0			
E. E. Turner	5	0	0			
H. Wren	10	0	0			
F. D. Chattaway	15	0	0			
G. W. Clough	5	0	0			
N. Dhar	5	0	0			
R. S. Morrell	10	0	0			
				137	0	0
,, Longstaff Medallist	20	0	0			
,, ,, Medal	1	10	0			
				21	10	0
,, Commission on Recovery of Income Tax				1	0	10
,, Advertisements				3	16	0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				297	13	6
				£461	0	4

I have examined the above Accounts with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant

23, QUEEN VICTORIA STREET, E.C.
March 2nd, 1916.

Approved—ALEXANDER PEDLER
A. LIVERSIDGE
CHARLES A. KEANE

The following is the list of Grants made for Research during the past year:

	£	s.	d.
Polymorphism of hydrazides and anilides. (Continued.) F. D. Chattaway	15	0	0
Relation between optical rotatory power and the relative configurations of optically active compounds. G. W. Clough	5	0	0
Reduction of mercuric chloride under the influence of light and other catalytic agents. N. Dhar	5	0	0
The corrosion of metals. (Continued.) J. A. N. Friend	5	0	0
Syntheses of benzo-γ-pyrones. B. N. Ghosh.	10	0	0
The Reformatsky reaction on benzylideneacetone and various substituted benzylideneacetones. A. T. King.	5	0	0
Synthesis of *iso*quinoline and its derivatives. F. A. Mason	10	0	0
Study of diazo-phenols. G. T. Morgan.	10	0	0
(*a*) Investigation on polymerised drying oils. (*b*) Oxidation of β-elæostearic glyceride. R. S. Morrell	10	0	0
Absorption spectra of organic compounds. J. E. Purvis.	20	0	0
Condensation of hydroxymethylene ketones with cyanoacetamide, cyanoacetic ester, and other substances. H. K. Sen-Gupta.	12	0	0
Chemical and physiological investigation of carnosine, etc. H. M. Spiers	15	0	0
The space formulæ of diphenyl and its derivatives. E. E. Turner.	5	0	0
Studies in the phenylsuccinic acid series. H. Wren.	10	0	0
Total	£137	0	0

A discussion took place with regard to the paragraph of the Report recording the action taken by the Council with reference to the question of removing the alien enemies from the list of Honorary and Foreign Members. A motion was proposed by Dr. G. T. Moody

> "That the Report now submitted be referred back to the Council, and that they be instructed to take immediate steps to remove the names of all Honorary and Foreign alien enemies from the Roll of the Society."

After a number of Fellows had spoken to this motion, Dr. L. T. Thorne proposed as an amendment:

> "That the paragraph under discussion be referred to the Council for reconsideration of the question of the removal of the names of the nine alien enemies from our Honorary Members."

This amendment was put to the meeting and carried, the original motion thus falling to the ground.

The adoption of the Report of the Council (with the exception of the following paragraph):

> "The question of removing the names of alien enemies from

> our lists of Honorary and Foreign Members and Fellows has engaged the anxious attention of the Council, who, by a large majority, decided that no steps can be taken in this direction, consistently with the dignity of the Society and with due regard to British ideas of justice, until after the cessation of hostilities."

together with the Balance Sheet and Statement of Accounts, was then put to the meeting and carried.

A vote of thanks to the Auditors, proposed by the TREASURER, seconded by Mr. JULIAN BAKER, was acknowledged by Dr. C. A. KEANE.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. J. A. VOELCKER and seconded by Mr. A. CHASTON CHAPMAN, acknowledgment being made by Dr. T. M. LOWRY.

It was decided to postpone the delivery of the President's Address, entitled, "Our Seventy-Fifth Anniversary," to the next Ordinary Meeting of the Society on April 6th.

The Report of the Scrutators was presented, and the President declared that the following had been elected as Officers and Council for the year 1916–1917:

President: Alexander Scott, M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President: Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Bailey Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents: Peter Phillips Bedson, M.A., D.Sc.; George Gerald Henderson, M.A., D.Sc., LL.D.; Charles Thomas Heycock, M.A., F.R.S.; Francis Robert Japp, M.A., LL.D., F.R.S.; Arthur Lapworth, D.Sc., F.R.S.; Richard Threlfall, M.A., F.R.S.

Treasurer: Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries: Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary: Arthur William Crossley, D.Sc., Ph.D., F.R.S.

Ordinary Members of Council: George Barger, M.A. D.Sc.; the Rt. Hon. the Earl of Berkeley, F.R.S.; Alfred Chaston Chapman; David Leonard Chapman, M.A., F.R.S.; Frederick George Donnan, M.A., Ph.D., F.R.S.; Charles Alexander Hill, B.Sc.; Kennedy Joseph Previté Orton, M.A., Ph.D.; Robert Howson Pickard, D.Sc., Ph.D.; Robert Henry Aders Plimmer, D.Sc.; Frank Lee Pyman, D.Sc., Ph.D.; George Senter, D.Sc., Ph.D.; Jocelyn Field Thorpe, D.Sc., Ph.D., F.R.S.

PRESIDENTIAL ADDRESS.

At the Annual General Meeting, March 30th, 1916.*

By Dr. Alexander Scott, F.R.S.

It is exactly seventy-five years to-day since The Chemical Society of London met for the first time in the rooms of the Royal Society of Arts after a preliminary meeting on February 23rd, 1841, had decided "*That it is expedient that a Chemical Society be formed.*"

At this first meeting the names of those who had consented to become original members of the Society were read, and two more were added before the first list was printed in the first number of the *Proceedings*, being seventy-seven in all.

Since that date the Society has met regularly on or about March 30th under a great variety of conditions, but never, with the exception of last year, in circumstances at all approaching those at present prevailing throughout Europe and over the entire globe.

The Crimean War in 1854–1856 is not even mentioned in the Reports of the Council or in the Presidential Addresses for these years, nor in still more recent times is the Boer War of 1899–1902 even referred to. These wars do not seem in any way to have awakened in our rulers any appreciation of the increasing part chemical science was destined to play in all warfare in the future.

On the other hand, the increased possibilities for the destruction of human life on a greatly magnified scale by the application of scientific methods had tended to make civilised nations regard war as well-nigh impossible. Most of us, I think, had ceased to believe that such a war as the present, with its absolutely reckless employment of human life as mere "Kanonen Futter," to use the barbaric but expressive nomenclature of our enemy, could occur amongst so-called civilised peoples, and, short of demonstration, we could never have believed that our own science could have been so utilised and prostituted for the furtherance of its unscrupulous aims by any cultured nation.

* The Address was delivered at the Ordinary Scientific Meeting, April 6th, 1916. Prof. J. M. Thomson proposed a vote of thanks to the President for the Address, coupled with the request that he would allow it to be printed in the *Transactions*. The motion was seconded by Sir J. J. Dobbie and carried with acclamation, acknowledgment being made by the President.

In the earlier years of the Society's life it seems to have been sufficient for the President to read the Report of the Council at the Anniversary Meeting, and sometimes the Report and the Balance Sheet, together with the appropriate headings, were contained on two pages of the *Journal*. Succeeding years have added considerably to what has been expected from the occupant of this Chair, and now at each anniversary meeting he is expected to deliver a formal address on some subject closely connected with the life of the Society as "a body politic and corporate," or on some subject of more purely scientific interest.

To-day, our seventy-fifth anniversary, suggests that the former of these subjects may fittingly form the theme of my remarks to you. Many thoughts arise in our minds on such an occasion, and lead us to reflect on the state of chemical science before the Society was founded, as to the aims and purposes for which it was deemed "that it was expedient that a Chemical Society be formed," and to examine the measure of success which has been achieved by the Society in fulfilling the objects of its founders, investigating any failures in the carrying out of these aims, and devising methods whereby its usefulness may be increased either along the old or along new and more effective lines. To assist us in this, a brief history of our Society and of its aims as set forth by many of my illustrious predecessors at various times and in divers manners may be useful at the present time when so many changes are in the air and when the British public seems at last to be awaking to the important rôle modern science, and especially our own department of it, plays, and must continue to play, in every branch of domestic, commercial, and national life. Therefore I venture to place before you these jottings from our life-history in the spirit expressed in the quaint words of the famous author of "The Sceptical Chymist": "Partly because I am not unapt to think that they may come abroad seasonably enough, though not for their author's reputation, yet for other reasons."

One of the letters received at the foundation of the Society was from Henry Fox Talbot, one of the pioneers in photography, in which he expressed the view that the science of chemistry alone was not sufficient to engage a society, and suggested a joint society for chemistry and electricity. How erroneous this view was is shown by the history of our own and similar societies.

The Chemical Society of London, as it was called when founded, is the oldest existing society devoted to the furtherance of chemistry, but within a month of its foundation the Pharmaceutical Society was formed, to be followed later on by the Chemical Society of Paris in 1858 and of Berlin in 1867, and by the American

Chemical Society in 1876. Even at home so vast has the field of chemical activity become that we have had to detach vigorous and flourishing offshoots from our own body, which, whilst working in perfect harmony with the parent society and containing many members of it, devote themselves to special branches. Of these I need only mention the Society of Public Analysts (1874), the Institute of Chemistry (1877), and the Society of Chemical Industry (1881).

Looking back to the times of the "father of chemistry and the brother of the Earl of Cork" (although I always have regarded him as the grandfather rather than the father of our Science) we wonder whether much progress has been made when we read in the "Introduction to the Sceptical Chymist," from which I have already quoted, "That of late chymistry begins, as indeed it deserves, to be cultivated by learned men, who before despised it; and to be pretended to by many, who never cultivated it, that they may not be thought to be ignorant of it:" A perusal of our Parliamentary and legal reports leads us to wonder how our legislators ought to be classed in accordance with the above statement, and to doubt whether the attitude of so-called learned men had done much more than "begin to change" during these two centuries.

It is not altogether without significance that the beginnings of this change, the foundation of the Royal Society and of the real initiation of the experimental method into true science by Robert Boyle and his contemporaries, followed closely on the Civil War and at a time when thoughtful men were striving once more to direct the energies of the country into peaceful and useful lines after the convulsions produced by military strife.

From the time of Boyle onwards for another hundred years or so the gradual substitution of careful experimental work in place of metaphysical speculations on the reasons for chemical and physical phenomena added much to the store of real knowledge. The rise and development of the phlogistic theory, the ingenuity of the theorems by which it was supported, and its final overthrow by the logical and brilliant experimental work of Lavoisier, illustrate this phase of the progress of scientific method.

My patriotic and perhaps grasping nature tempts me oftentimes to think that, without unduly sacrificing truth, the famous claim of Wurtz that "Chemistry is a French science founded by Lavoisier of immortal memory." might be paraphrased by changing "French" into "Scottish," and substituting "Black" for "Lavoisier." There can be but little doubt that the great progress in chemistry dates from the experimental research of Joseph Black in 1755 on "Magnesia alba," and his introduction of the chemical balance as the supreme arbiter on matters of chemical change. Chemistry then

became an exact and quantitative science, and by means of the balance all changes and reactions and the rearrangements of matter could be traced with certainty, new elements and new compounds discovered, and new laws of nature revealed.

Lord Brougham, who attended Black's lectures, in his "Philosophers of the Time of George III.," claims that "The physical sciences have few more illustrious names to boast than that of Joseph Black." He had "the good fortune of opening to mankind new paths in which both himself and his followers successfully trod, enlarging to an incalculable extent the bounds of human knowledge." This was due to "the happy union of strong but disciplined imagination with powers of close undivided attention and ample resources of reasoning which forms original genius in scientific pursuits." "His modesty in publishing his speculations and his genuine devotion to the investigation of truth for its own sake led to his incontestable claim to be regarded as the founder of modern chemistry being oftentimes overlooked."

Black was one of the earlier members of a galaxy of brilliant investigators who flourished from about 1750 through the turmoils of the time of the French Revolution and the European wars which culminated in Waterloo. In those war-stricken times, as at present, although to a much more limited extent, the vital importance of chemistry to the national life, and even to its very existence, was plainly demonstrated, but, as now, was recognised much more clearly by our adversaries than by ourselves. Witness the invention of the Le Blanc soda process in France, which was destined, however, to do more for us than for anyone else, leading to an enormous increase in our chemical manufactures and trade, extending, with its ramifications, to the present day as the "heavy chemical trade." The beet-sugar industry and the methodical production of nitrates further indicate how clearly Napoleon grasped the situation and strove to render France independent of England and her colonies.

A century ago chemists in this country were vigorously at work, and epoch-making discoveries, both in theory and in practice, were the natural outcome. The atomic theory of Dalton, the isolation of potassium and sodium by Davy, and his proof that chlorine was an element, date from the early years of the nineteenth century, to be followed by the discovery of benzene and of the liquefaction of chlorine and other gases. These apparently useless discoveries were destined at a later date to become the starting points of vast industries.

In these early days discoveries in chemistry found a means for their dissemination chiefly through the medium of the *Philosophical*

Transactions of the Royal Society, and the investigations themselves were discussed at the meetings of the Society. Just as the Royal Society grew out of pre-existing societies, in which the social element was blended to a very considerable extent with the scientific, so our own Society had as forerunners "The Tepidarian Society" (of 25), which drank only tea, and met at Old Slaughter's Coffeehouse in Saint Martin's Lane, a society of which Davy was a member, as he was also of the Animal Chemical Society (of 12), of which another member was Brande. In 1806 an attempt was made to found a Chemical Society, but it was not a success, being frowned on by Sir Joseph Banks, President of the Royal Society, who feared that "these various new-fangled associations will finally dismember the Royal Society, and not leave the old lady a rag to cover her."

Davy refers in a letter to W. H. Pepys dated November 15th, 1807, to the Chemical Club: "Some things have happened in the Chemical Club which I think render it a less desirable meeting than usual, and I do not think you would find any gratification in being a member of it. . . . We sometimes meet only two or three" (Paris, "Life of Davy," Vol. I., p. 279).

The British Association for the Advancement of Science was founded in 1831, and brought together scientific men domiciled in various parts of the country, and at its annual meetings sorted them out into groups according to their own specific subjects. In this way the chemists in Section B assembled to discuss their various investigations and the difficulties met with in their prosecution before proceeding to the formal publication of their work. These meetings, from their helpful nature, no doubt suggested the formation of a formal and central Society ten years later, the chief object of which would be the communication and discussion of chemical papers. I refer later to the assistance given by the Association to our Society in its earlier days in the form of grants to enable abstracts of foreign papers to be published.

At a later date the meetings of Section B led to the founding of another chemical society or club (or "hive" of B's as they sometimes styled themselves). Our Library possesses some of their compositions, and I have come into the possession of several others, along with an album containing photographs of several "B's" dating between 1865 and 1870, no doubt during the period when Dr. W. J. Russell was its secretary. These I propose to present to the Library, and I hope that any Fellows of the Society or their friends who may possess any relics of this interesting small Society may assist in rendering as complete as possible our collection of its records. The Club was limited to twenty members, who united to

[To face p. 343.

their devotion to chemistry a strong conviction that in addition to the objects set forth in our Charter and the best means of fulfilling them, there were other ways of promoting the welfare of chemical science than those contemplated by the more formal Society. They therefore dined together once a month during the Society's session, and in the summer an excursion was made into the country, guests being invited. The following was the invitation form for guests:—

Hope that.....

will join them at their Meeting on the 31st of March at the

RAINBOW TAVERN, FLEET STREET.

DINNER AT 6 O'CLOCK PRECISELY.

Reply is requested, to Dr. W. J. RUSSELL, 34, Upper Hamilton Terrace, N.W.

and the "sort of crowd," as the Americans would say, who assembled is well shown by the signatures opposite.

That they discussed in a duly reverent spirit the theories then before the chemical world is shown by the illustrations of the competing graphic notations given on page 344.

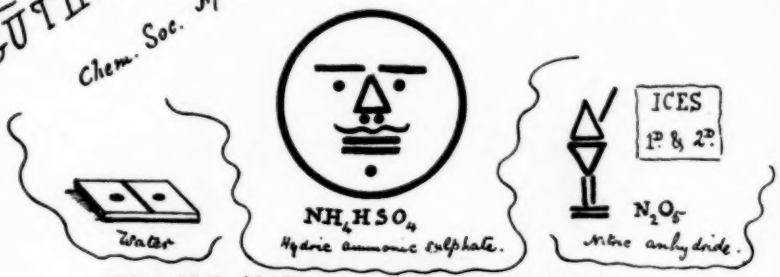
There were several poetic spirits who proved that there is no real hostility between a literary training and the scientific spirit. The poets-in-chief were Frederick Field, John Cargill Brough, and William Phipson Beale, and it is to Sir W. P. Beale that I am indebted for much information concerning the B's, and have been able to record the authorship of some of these *jeux d'esprit* with certainty. His recent book on crystallography presented by him to the Library on its publication last year shows that, besides his many-sided Parliamentary work, he is still a busy B and making honey of the true kind. Only two B's besides himself remain so far as I can find out, namely, Professors Odling and G. Carey Foster.

I think some of the poems are too good to be hidden even in

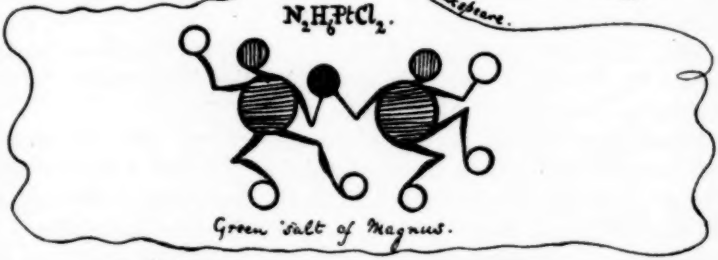
GRAPHIC FORMULÆ

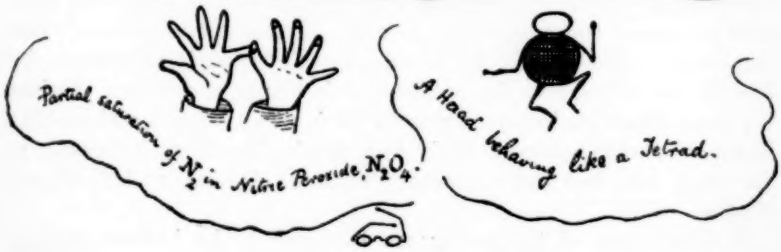
GUTHRIE

Chem. Soc. April 16, 1868. $H = \bullet$, $O = —$, $S = \sim$, $N = \triangle$.



FRANKLAND AND CRUM BROWN.





our own Library, and so give two specimens, as well as one of the notices regarding a country excursion:—

ON THE UTILIZATION OF SEWAGE BY PHOSPHATE OF ALUMINA.

A PAPER WHICH OUGHT TO BE SUNG TO THE B CLUB

BY

D. FORBES, F.R.S., AND DR. ASTLEY PRICE.

THE CLEARANCE OF THE WATERS.

There is not in the wide world a water so sweet
As the effluent liquid when sewage we treat:
Oh! the last trace of organic foulness departs
With the charm our alumina phosphate imparts.

We reck not that Nature has shed o'er these drinks
Her foulest of products, her vilest of stinks,
To pollute the soft magic of streamlet or rill;
We make them salubrious and exquisite still.

We render the water as wholesome as beer,
And make each dear ton of the solid more dear;
And thus we the best charms of nature improve,
And $Mg_2\ NH_4\ PO_4$ remove.

Sweet alumina phosphate, how calm could we rest
By the side of a drain with the drink we love best,
If Bazalgette, Hawksley, and Denton would cease,
And our stuff with the sewage were mingled in peace.

MODERN CHEMISTRY.

I'm all in a flutter; I scarcely dare utter
The words I have set to a jingle;
For I see at this table philosophers able,
Whose ears at my verses will tingle.
Still, I don't mind confessing, I'm fond of expressing
My notions and thoughts, in defiance
Of every great gun who can't see the fun
Of winnowing chaff out of science.

I've read till I'm weary books weighty and dreary
In which certain chemists seem aiming
To prove to outsiders they're excellent riders
Of hobbies in theory and naming.
With "monads" and "diads," and "pentads" and "triads,"
My brain has been addled completely;
And what's really meant by "something-valent,"
Is a question I give up discreetly.

Though Frankland's notation commands admiration,
As something exceedingly clever,
And Mr. Kay Shuttleworth praises its subtle worth,
I give it up sadly for ever:
Its brackets and braces, and dashes and spaces,
And letters decreased and augmented
Are grimly suggestive of lunes to make restive
A chemical printer demented.

I've tried hard, but vainly, to realise plainly
Those bonds of atomic connexion,
Which Crum Brown's clear vision discerns with precision
Projecting in every direction.
In fine, I'm confounded with doctrines expounded
By writers on chemical statics,
Whom jokers unruly may designate truly
As modern atomic fanatics.

I turn for instruction to Brodie's production,
But stick at the famous equations
Which make chlorine fare as "alpha ki square,"
Or the product of three operations.
It may be the case that the "unit of space"
Requires symbolic expression;
But I cannot extract any notions exact
From Sir Benjamin's daring aggression.

For years I received the doctrines believed
About acids with much satisfaction,
And constantly swore H_2SO_4
Was an acid above all detraction;
But Williamson's views my notions confuse,
And make me once more undecided
Whether old SO_3 the acid should be,
Or merely a fragment divided.

When Odling with unction dilates on a function,
I sink out of sheer inanition;
For I find his "aplones" and "diamerones"
Indigestible mental nutrition.
In fact, I am dazed with the systems upraised
By each master of chemical knowledge,
Who seems to suppose that truth only grows
In the shadow of one little college.

J. C. B.

March, 1868.

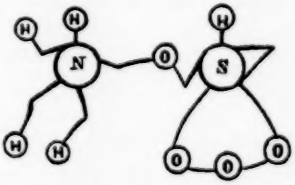
ILLUSTRATIVE GRAPHIC FORMULÆ.

Acid sulphate of ammonium, NH_4HSO_4.

According to Guthrie.

[N=Δ H=· S= ..... O=–]

According to Frankland.



[Here N is seen to be a pentad and S a hexad.]

"Come, fill up your glasses as high as you can,
For each of the Bees is a jolly good man,"
&c. &c.

RED LION COURT,
June 9, 1875.

DEAR SIR,

At the request of our worthy Secretary **B** Beale, I beg to inform you that the COUNTRY EXCURSION of THE BEES is fixed for the 19th, at Mickleham. Considering the unusual circumstances attending this Meeting, **B** Nicholson having promised to supply the finest Veuve Cliquot, **B** Müller some choice sparkling Rheinwein, **B** Van Voorst some extraordinary Sherry, and **B** Francis some 1857 Neroberger, it is expected that the swarm will this year be an unusually large one. You are therefore requested to inform the Secretary as early as convenient whether it is your intention to be present, and what number of friends, if any, you will bring with you, in order that a sufficient supply of food be prepared.

I may also mention that it is expected that **B** Reekes will bring with him his celebrated compass, and will guide us by the most indirect route to the Running Horses, and that **BB** Beale and Holzmann will have with them copies of the latest edition of the Leipziger Commerz-Buch, so that the woods and glades may again resound with a merry hum, as in olden days. For those more addicted to prose, it is hoped that **B** Forbes, if not collecting honey in Spain or Russia, will have a store of new original tales and anecdotes.

Gaudeamus igitur!

Yours truly,

W. FRANCIS.

For TRAINS *see over.*

TRAINS LEAVE:—

BY SOUTH-WESTERN.

Waterloo.....	**11.20**	**1.30***	3. 0
Clapham Junction...	11.32	1.42	3.10

* Reaches Leatherhead at 2.16.

BRIGHTON AND SOUTH COAST.

London Bridge.....	**2.0†**	2.18	3.20

† Reaches Leatherhead at 2.49.

BY SOUTH-EASTERN TO BOX-HILL.

Charing Cross	**1.5**	2.15	3.28
Cannon Street	1.17	2.23	3.38
London Bridge	1.20	2.26	3.41
Croydon	1.38	2.46	4. 0

Observe! Those proceeding by the 11.20 train will lunch at *Leatherhead*, and wait there the arrival of the 1.30 train.

DINNER AT 4.45.

MEETINGS OF THE

B S.

RAINBOW TAVERN, FLEET STREET.

1869–70.

Tuesday, November	2
——— December	7
——— February	1
——— March	1
——— April	5
——— May	3

Dinner at 6 o'clock punctually.

MEMBERS OF THE CLUB.

C. Abel.
F. A. Abel.
W. P. Beale.
E. F. Best.
F. Field.
D. Forbes.
G. C. Foster.
M. Foster.
W. Francis.
M. Holzmann.
A. Matthiessen.
H. Müller.
H. M. Noad.
W. Odling.
A. P. Price.
T. Reeks.
W. J. Russell.
J. Van Voorst.

The rules of the Club, headed by the appropriate emblem, were printed, as were also the card with the dates of the meetings for the session and the list of B's.

The successor to the B Club is the Chemical Club, and though it issues no rules or lists of members, flourishes under the energetic secretaryship of Professor H. E. Armstrong with a nominal membership of fifty.

Fellows present may like to have some idea of the personal appearance of the founders of our Society, and I have been able to project upon the screen what to me is the most striking portrait of Thomas Graham, our first President, I have seen. I owe this to the kindness of Professor J. M. Thomson, who has had the courage to entrust to me for the purpose of making the transparency the negative from which he prepared the exquisite platinotype print in the Jubilee Album. The Society realises but little how much it is indebted to Professor Thomson's care and energy for the portraits of the Past-Presidents in the Council Room and the priceless series of platinotype prints in the Jubilee Album. The only record of what he has done in this direction is a sentence on page 18 of the Jubilee Volume, which states that of the forty-four portraits in the Album more than half have been executed by Professor Thomson, of King's College. I believe it would have been more correct to have stated that nearly the whole of them were due to him.

[The portrait of the first Secretary, Robert Warrington, which hangs in the Officers' Room, was also exhibited.]

To return to the foundation of the Society itself, it is interesting to note that from its very foundation it has laid stress on the importance of research, and president after president has insisted that, however it may seem to flourish financially or in other worldly ways, it is on the amount of research and on the vigour with which that is prosecuted by its Fellows that the reputation and the true value of the Society must always depend.

In the statement of the objects to be aimed at by the Society as amended at its meeting on March 30th, 1841, we find that the establishment of a "Laboratory of Research" is specifically mentioned as one of the ulterior objects of the Society, in addition to a Museum and Library, and the communication and discussion of discoveries and observations.

At the first anniversary meeting the Report of Council states: "The Council is fully sensible that the utility of the Society and its reputation in the scientific world will mainly depend on its publications" (1842).

Again in 1845 the Council recognises it as a serious duty devolv-

ing on it to stimulate and encourage the zeal of the members by every means in their power, and recognises that there should be no unnecessary delay in the publication of papers, and that by pressing somewhat unreasonably on the time and goodwill of the Secretary six numbers of the "Memoirs and Proceedings," consisting of forty communications, had been *published during the year.*

Curve showing the growth of the original communications published in full by the Society from 1841 to 1915.

The thin line in steps shows a series of averages for periods of seven or of eight years.

The Memoirs and Proceedings had been published at intervals according as materials came to hand, and it ought to be noted that several very important investigations were embodied in these early volumes, a fair number of which were carried out on the Continent. The first paper read at the first scientific meeting on April 13th, 1841, was entitled, "On the Preparation and Formation of Yellow Prussiate of Potash," by Professor Liebig. The first volume contains papers, "On the Atomic Weight of Carbon," by Redtenbacher and Liebig; "On the Radical of the Cacodyl Series of Compounds," by Bunsen, as well as several by Ure, Stenhouse, Graham, and Fownes.

In 1848 the *Quarterly Journal* took the place of the Memoirs, and with it began the regular publications of the Society, which have continued ever since. In this year also the Charter of Incorporation was granted to the Society by Queen Victoria "*on this second day of November, in the 12th year of our reign*," when "The Chemical Society of London" became "THE CHEMICAL SOCIETY."

I have already stated that no mention of the Crimean War occurs in our records, but it is interesting to note that in 1854 the Council decided that lectures not exceeding five in number in any year should be given, and in making this arrangement to increase the interest in the scientific meetings the opportunity was again seized to impress on Fellows that it was not in the interesting nature of the meetings, but solely on its publications, that the position and character of the Society would depend.

In the report of the following year a sentence occurs which is equally true now, and may again be commended to the notice of Fellows, namely, "That the Library is a place of deposit for curious works upon Chemistry, and for pamphlets upon chemical subjects, which, collected, are of great interest, but, separately, are often of little or no value to their possessor."

Although discovered in 1856, a substance which was the forerunner of a multitude of others from the same source and the origin of a vast industry which we hope may once more be ours was first exhibited, together with some other coal-tar products, on March 31st, 1857, to the Society, which then occupied its first set of rooms in Old Burlington House, where the Royal and Linnean Societies were also located. This was followed next year by a change in the day of meeting from Monday to Thursday, so that all three societies might meet on the same day.

The Library had now (1860) become such an important part of the Society's possessions that a permanent librarian was appointed in the person of Henry Watts (whose portrait also has been brought here from the Officers' Room), a name known and reverenced by all who wanted to know anything that was to be known in chemistry as long as he maintained his connexion with the Society, not only as its Librarian, but as the Editor of its *Journal*, a connexion that was only terminated by his death. He was elected Editor in December, 1849, and died in June, 1884. To those who use his Dictionary (I mean the original and vigorous edition) it is rather quaint to find it recorded that the office of Librarian "has been undertaken by Mr. Watts, a gentleman who is familiar with the literature of the Science."

In 1862 the Society attained its majority, when its Fellows had

increased from the original 77 to 360. Hofmann, then President, was able to declare that "By the number of our body, by the value of its contributions to Science, by the increasing interests which our proceedings elicit we have secured a respectable position in the world. We may look with some degree of satisfaction upon the achievements of our youth, and from the result of the past derive encouragement for the future."

The International Exhibition in Hyde Park held in 1862, amongst its many benefits was not without an influence for good on chemistry and the Chemical Society. It brought many Foreign Members into personal contact with the Society to which they had been elected for their pre-eminence in the advancement of our Science. It likewise brought about the delivery of lectures in their own language on "Vapour Densities," by St. Claire Deville on May 15th, and by Wurtz on June 5th; on "Oxide of Ethylene considered as a link between mineral and organic chemistry."

In 1862 appeared the first volume of what was termed the "New Series" of our *Journal*, which was published in monthly numbers, as now. For many years past the numbering of the volumes has been that which reckons Volume I. of the Quarterly Journal as the true starting point of our regular publications, those for the present year being Volumes CIX. and CX., because in each year since 1876 two volumes have been published, of which since 1878 one is Transactions, that is, papers presented originally to us for publication, and the other abstracts of work done elsewhere throughout the world.

The lectures delivered by our two French *confrères* had an important effect on our Society beyond even what Hofmann eloquently voiced in the following words: "In establishing once for ever these international chemical discourses at its meetings the Chemical Society has loudly proclaimed the cosmopolitan character of Science, and that henceworth it will look upon the several nations engaged in scientific pursuits as upon so many federal States of a great republic united by love of science and pledged by contributions to a common treasury as it were, to uphold its cause and raise its dignity." The commencement of lectures so successfully made in this way by distinguished foreigners undoubtedly directed the ideas of the Council and those who desired to perpetuate in a fitting manner the name of one who for his personal gifts as well as for the great extension of chemistry and physics has left his impress on science for all time. Although one of the original Fellows, he could never be induced to become the President of the Society. His name and memory will ever be kept green by the

foundation of the Faraday Medal and Lectureship which was founded in 1869. To the institution of this we owe many notable discourses, which on each occasion, thanks to the kindness of the Managers of the Royal Institution, have been delivered in the same lecture theatre and from the same spot where Faraday had so often held audiences enthralled by the spell of his eloquence, enthusiasm, and perspicacity. It is not generally known that the first six Faraday Medals were of palladium, of which precious metal in 1870 Messrs. Johnson and Matthey presented £200 worth for the purpose, and it was hoped that this would be sufficient to make the first ten medals.

Professor (afterwards Sir Edward) Frankland's address in 1873 contains much that is of peculiar appositeness at the present time, and shows how slowly methods in education move. After referring to the gratifying increase in the number of original communications made during the year to the Society, the President went on to say: "It must not be for a moment imagined, however, that we have in this important matter taken the position which we undoubtedly ought to occupy as the nation holding the first place in wealth, trade, manufactures, and State revenue. The statistics of experimental discovery show that we are at present very far from the attainment of such a position. I have on a previous occasion expressed the opinion that the chief cause of this deplorable result is the non-recognition of experimental research by our universities. Further inquiries into the conditions under which degrees and honours in experimental science as given here and elsewhere have only served to deepen my conviction that the progress of physics, chemistry, and biology is intimately bound up with the nature of the training prescribed by the governing bodies of universities for students of these sciences; and that until a profound change is made in the awarding of prizes and the granting of degrees in science in this country, we shall look in vain for any substantial improvement in the prosecution of experimental investigation."

He then went on to remark on the offering in 1874 of a Fellowship at Trinity College, Cambridge, for proficiency in natural science, in which great weight would be attached to the original dissertations sent in by the candidates that "such an innovation in the award of Fellowships will be followed with great interest by all who have the progress of scientific discovery at heart. Let us hope that it will inaugurate a new era in the university life of this country."

His words require no apology for my repeating them here, and they indicate how much behind the times the older universities have been in their movements in educational matters. They have

undoubtedly done much since 1873, but they have not moved at anything like the rate necessary to enable them to make up the heavy lee-way of those days, and so take the lead in matters in which it is their function and their duty to direct progress.

In 1874 we entered into possession of the rooms we now occupy, but which in 1892 were rearranged as they now exist. The changes introduced at this later date were the re-seating and rearrangement of the meeting room, and attempts to improve its ventilation which, with some further modifications effected at a very recent date, still leave something to be desired.

The preparation by Mr. Watts of the first volume of the Collective Indexes is recorded this year, and covers the period 1841–1872.

In the following year a careful discussion of the financial position of the Society is given, and the growth of the income was considered to be such as to warrant the hope that the Society would be able to dispense with the aid it received from extraneous sources for the purpose of publishing the abstracts from foreign journals. For some years the British Association had given £100 a year, and Fellows had in some years contributed as much as £250, so that this might be done satisfactorily.

In 1876 the admission fee was raised from £2 to £4, but I am glad to say that the annual subscription remains to-day the same as it was fixed seventy-five years ago for Fellows resident within twenty miles of London, namely, at £2. Long may it continue to do so.

The selling price of the *Journal* was raised to £1 10*s*., at which price it remained until 1895, when £2 was fixed as its price, and owing to its ever-increasing size and cost last year it was found necessary to raise the price to £3.

The Society never succeeded in possessing a Research Laboratory of its own, such as it desired to do in 1841, owing largely to the numerous laboratories and facilities for research having increased. Proposals by Mr. T. Hyde Hills in 1872 to form a Fund for making grants in aid of research came to nothing until in February, 1876, Dr. G. D. Longstaff stated that he was willing to give £1,000 to the Society to be invested and the interest expended in the promotion of chemical research provided that another £1,000 could be raised and applied to the like purpose. A committee was formed and set to work with such purpose that a sum of £1,042 7*s*. 0*d*. was collected before the meeting of Council on December 21st. This was exclusive of a donation of £1,000 from the Worshipful Company of Goldsmiths, and at the next meeting of Council on January 18th, 1877, Dr. Longstaff presented the transfer of £1,000 North British 4 per cent. preference stock in fulfilment of his promise.

Other City Companies which assisted the Fund were the Drapers' Company, who subscribed 100 guineas a year for three years, and the Clothworkers', the Merchant Taylors', and the Mercers', who each gave donations of 100 guineas.

In its final report in April, 1877, to the Council, the Longstaff Committee, as it was called, reports that less than £100 has been received since the issue of the circular in February (Jubilee vol., p. 204). The circular points out that the first list of subscribers are principally scientific chemists, and that with very few exceptions chemical manufacturers have hitherto abstained from aiding this Fund.

The Research Fund within three years of its foundation amounted to more than £4,300, and continued to receive donations, so that at the time of the Jubilee celebration its capital amounted to a little short of £6,000.

The usefulness of the Library was very greatly increased by the decision of the Council to obtain duplicate sets of the more important serials so that these might be available for circulation, and this policy, initiated in 1879, has been maintained ever since, and, thanks to the beneficence of the late Sir Henry Roscoe and others, our Library occupies in this respect a unique position.

During Sir Henry Roscoe's presidency the Faraday lecture by Helmholtz was delivered. The Society of Chemical Industry was also founded, and a Royal Commission on Technical Instruction was appointed by the Government, of which our President was a member, and in his address in 1882 gave an account of its work.

A very interesting comparison of the opportunities for instruction in pure and applied chemistry was given by Sir Henry Gilbert when he gave an account of those available when he was a student, and contrasted them with what he had seen, not only in this country, but also during a visit to Canada and the United States.

In 1885 the Proceedings were issued as a separate publication and in a form suitable for the publication of preliminary notices of work and short notes on various subjects, and contained abstracts of all papers read before the Society.

Sir W. H. Perkin and Dr. Hugo Müller, like many of their predecessors, dealt in forcible terms with the lack of encouragement of research and the absolute necessity of high scientific training for those engaged in scientific industries, and their addresses well repay careful perusal, for no two men were ever so fully entitled and qualified to speak authoritatively on the subject.

It was at the end of Dr. W. J. Russell's first year of office that the Anniversary Meeting was held for the first time in the after-

noon, and after the meeting the Fellows dined together, a custom which has been kept up by, not an annual, but a biennial, dinner, with few exceptions, ever since until the present War, to be resumed again, we hope, in happier times.

An event of great importance in the history of the Society was the celebration in 1891 of the Jubilee of its foundation, which consisted of an afternoon meeting when addresses were delivered and delegates received from many learned societies at home and abroad; an evening reception and *soirée* in the Goldsmiths' Hall, where an exhibition of historical and of interesting apparatus and specimens was shown, and finally a dinner on the succeeding evening, attended by the Marquis of Salisbury, then Prime Minister, and other distinguished guests.

During the presidency of Professor Crum Brown the first of the memorial lectures, on the life and work of Jean Servais Stas, from the pen of the late Professor Mallet, was given, to be followed after a brief interval by one on Hermann Kopp by Sir Edward Thorpe, to whose ready pen and sympathetic treatment we owe so many of the later memorial lectures.

The Faraday Medal was presented to Lord Rayleigh for his work on the discovery of argon at the close of Professor Armstrong's term of office in 1895, and the meeting was rendered still more memorable by Sir William Ramsay's account of the discovery and preparation of helium from cleveite, Sir William Crookes giving an account of the spectroscopic evidence proving its identity with that of the element in the atmosphere of the sun.

In 1898 the Society entertained to a banquet six of its Past-Presidents who had been Fellows of the Society for fifty years, namely, F. A. Abel, E. Frankland, J. H. Gilbert, J. H. Gladstone, W. Odling, A. W. Williamson. The celebration was originally fixed for June 8th, and it was confidently hoped that the last survivor of the original members of the Society, Lord Playfair, who was President in 1857–1859, would have been present, but his death on May 30th disappointed all, and led to the postponement of the dinner until November 11th.

A second celebration of the same kind was held on November 11th, 1910, when the following five Past-Presidents were invited to be the guests of the Society, namely, W. Crookes, A. G. V. Harcourt, H. Müller, W. Odling, H. E. Roscoe, and of these one had been entertained at the earlier banquet and happily is still with us.

The advent of the new century was fitly marked by Sir Edward Thorpe giving a most interesting historical account of chemistry from the beginning of the past century up to the foundation of the Society. In 1901 the death of Queen Victoria, whose beneficent

reign began a few years before the foundation of our Society, led Sir William Tilden in 1904 to complete, with his well-known skill, the modern history of chemistry by giving a summary of the progress of chemistry during the Victorian era. The Society also owes to Sir William Tilden the initiation of the Annual Reports on the Progress of Science, of which twelve volumes have now been published. Thanks to the self-sacrificing labours and energy of those of our Fellows who take part in their preparation, they are justly regarded as the most complete in their way, and are unique both from the promptness with which they are published and the ground they cover.

The Celebration of the Jubilee of the discovery of mauve and of the coal-tar colour industry fell most opportunely during the Presidency of the late Professor Meldola, to whose untiring energy and profound knowledge of the subject and everything connected with it the great success of the celebration was largely due. In acknowledging the address presented by the Chemical Society, Sir William Perkin mentioned that for seventeen years he had been a Secretary of the Society, and for two years its President. When mauve was discovered in 1856 the membership was 261, and in 1906 it was 2,700. To the subscribers to the Perkin Fund we owe the marble bust which adorns our Library, as well as an addition of £2,704 3*s*. 8*d*. to our Research Fund, which a few months before had received a second donation of £1,000 from the Worshipful Company of Goldsmiths. These have raised the annual income of the Fund almost to £350, which is still far from sufficient to meet the many applications worthy of support in the way the Research Fund Committee and the Council would desire. I am glad that the addition of £2,500 to the Fund which I have been privileged to announce to-day will assist the Council in making somewhat larger grants to those who so richly deserve every encouragement which our Society can give.

In these somewhat scrappy notes in which I have dealt with the earlier part of our history more fully than in the later, one association deserves mention, though its activities are now paralysed. I refer to the formation of the International Association of Chemical Societies, which met for the first time in Paris in 1911, then in Berlin in 1912, and although it was arranged that it should meet in London in 1913 various circumstances arose which led to the meeting being held in Brussels. Amongst the reasons for the change of meeting place was the unconditional gift of 250,000 francs by M. Ernest Solvay, as well as of an annual income of 37,500 francs and of a handsome set of rooms in the Solvay Institute there for the permanent offices of the Association. For obvious

reasons no meetings were held in 1914 and 1915. I fear that the offices and all the documents and endowments are at present in the hands of the Huns. Any meetings in the immediate future are not likely to be of the same international and harmonious character as those of the past have been.

As I have already indicated, the importance of stimulating and encouraging research was recognised from the first by the founders of our Society, and President after President has insisted not only on its absolute necessity if we are merely to hold our own in commerce and manufacture, but that it must be strenuously cultivated by securing for this purpose the highest talent and the best brain power if we are to make any progress. The making of discoveries and the wresting from nature of her secrets is the paramount duty of every scientific man. This is agreed to tacitly by all, but tacitly it still remains. This negative or neutral attitude is maintained partly because the public in general, and in a more especial degree the so-called well-educated classes who have been to public schools and the older universities, have no conception of what research means. The classical scholar pure and simple adds but little to the sum of human knowledge. He turns over and over again that which has been accumulated in past ages extracting what was buried by those who went before and who did make some real progress worth recording. He always puts me in mind of a ploughman, say, on the field of Waterloo who may find a leaden bullet really fired from a musket a hundred years ago (and not planted since). He wonders which side fired it, whether it hit anyone, and many other such problems arise in his mind, all of which may be perfectly legitimate objects of inquiry and require much ingenuity for their complete solution. They may even be of considerable interest to the anxious inquirer, but of what use can they be to anyone? The classic may retort of what use are many of your chemical researches to anyone. The reply is that "Knowledge is power." Every addition to our knowledge, be it of a new element, a new compound, a new reaction, or a new law of nature, all such knowledge increases the power to make still further advances and confers a greater power to overcome difficulties, and in the end to increase human happiness and the advancement of civilisation.

Let us take some simple examples of what research has done in the past such as everyone can appreciate, and realise the connexion between the quest of knowledge for its own sake and the results of the application, it may be many years afterwards, of the knowledge so discovered, to the manufactures and requirements of the present day.

For this purpose we may divide research into two distinct categories, each of which requires for its successful prosecution a different type of mind and training.

The devotee of the first type seeks the mere addition of fresh knowledge to that already recorded, fresh ways of overcoming natural difficulties, new ways of utilising energy and of directing it. The second type starts on the definite quest for the solution of a determinate problem; it may be the building up of some compound occurring in nature, the profitable extraction of a metal from its ores, or the preparation of a substance which shall have definite properties.

Many examples of these are known to all present, but perhaps as "The Sceptical Chymist" would remark, "it may well be for divers reasons that some of them be recorded here."

Researches of the first type may well be exemplified by the experiments of Cavendish in 1785 on the composition of the atmosphere when he converted the nitrogen and oxygen into nitric acid, proving that it was formed, but required more oxygen to be added, and at the same time recording that a small residue of some gas remained uncombined, "so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid we may safely conclude that it is not more than 1/120th part of the whole." This discovery lay dormant for more than a hundred years until Lord Rayleigh proved that pure nitrogen prepared from a compound was lighter than the so-called nitrogen from the atmosphere which led in his and Sir William Ramsay's hands to the detection and isolation of argon, the first element of a type hitherto unknown in that it seems to have physical without chemical properties, and other members of the same group were shortly afterwards discovered and separated from the atmosphere and other sources. Lord Rayleigh's method of preparing argon from the air was but a modification of Cavendish's original experiment, but it led incidentally to his making a determination of the amount of energy required to prepare nitric acid from air and oxygen. In his presidential address to the British Association at Bristol in 1898 Sir William Crookes, with his usual perspicacity and directness, pointed out what *must* happen if the population of the world went on increasing at the rate it was then doing, and that the only means of averting certain catastrophe was to obtain the nitrogen of the air in a form suitable for plant life before the supplies of natural nitrates should be completely used up. The experiments of Cavendish and of Rayleigh now gave a theoretical clue to one solution at least of the problem. A great industry has grown up, although

not in this country, where these discoveries were made, but in Norway, Switzerland, and America, in which atmospheric nitrogen is converted into calcium nitrate and nitrite.

Similarly, Moissan's investigations into reactions which take place at temperatures producible by means of the electric furnace led to the discovery of many new compounds, of which the carbides, compounds of the metals with carbon, were soon shown to be of high technical importance. One of them, the well-known calcium carbide, was found to yield practically pure acetylene on treatment with water, and for this purpose it is manufactured in quantity. Other reactions, such as the formation of cyanides in blast furnaces, previously observed by Dawes in 1835, were proved by Bunsen and Playfair to be dependent on the atmospheric nitrogen, and led to experiments being made with calcium carbide and nitrogen. The reaction, although not giving a cyanide, gave calcium cyanamide, from which either ammonia or cyanides can readily be obtained. In these industries the original experiments on which they are based were made solely with the object of increasing our knowledge both in extent and in accuracy, but, without much further research of an accurate and often apparently useless nature, these could never have been brought to a successful conclusion on a practical scale. The effects of temperature and pressure on the rate and the extent of combination of the oxygen and nitrogen had to be determined, and also in the carbide process the effect of adding various salts to the mixture of lime and carbon, as well as to the carbide produced, to find out whether these might increase the rate of combination of the nitrogen either by some surface action or by rendering the mass more porous or by permitting the action to go forward as a lower temperature.

Important and interesting from the philosophical aspect in view of the theories as to the constitution of salts then being discussed, as were the experiments on the decomposition of water by Nicholson and Carlisle and of the alkalis by Davy, the part which these researches were to play in their application to the arts at no distant date was but dimly realised. Davy in 1826 remarks "that the true origin of all that has been done in this department of philosophy was the accidental discovery by Nicholson and Carlisle of the decomposition of water by the pile of Volta on April 30th, 1800, which was immediately followed by that of the decomposition of certain metallic solutions and by the observation of the separation of alkali on the negative plates of the apparatus."

Sodium is now manufactured by tons by Davy's process of electrolysing sodium hydroxide, as is calcium from calcium chloride.

The electroplating and electrotyping industries depend on the same electrolytic decomposition of metallic salts for their success. Hydrogen, oxygen, and chlorine are all similarly prepared. From Faraday's experiments made in the same laboratory on liquid chlorine and other liquid gases another industry has grown up, whilst his discovery and separation of benzene from oil gas has originated one of the most interesting and the most complex of all the chemical industries, which has its origin in the manufacture of coal gas and the separation from that and its by-products of a whole host of similar compounds and their transformation into dyestuffs, perfumes, drugs, and explosives. Even now there seems to be no limit to the possibilities still latent in coal-tar, that smeary mine of untold wealth both as hard cash and in chemical theory.

Of victories due to the second type of research no better examples could be given than the investigations which led up to the preparation on a manufacturing scale of alizarin, the colouring matter of madder root, and of indigo, which is derived from many leguminous plants grown for its sake in India, China, and elsewhere. Alizarin was proved to be closely related to anthracene, a solid which existed amongst the by-products of coal gas and along with naphthalene was at one time considered a nuisance as tending to choke the gas mains by being deposited in them. The naphthalene, for a long time of but little value, is now utilised in making indigo and other dyestuffs. Indigo was known to be closely related to aniline in 1826, and other syntheses besides that from naphthalene are based on a knowledge of this. By the manufacture of these dyes from coal-tar products millions of acres of land are set free for the growth of other crops. Before accomplishing the feat of manufacturing indigo at a price which could compete with indigo from the plant, the Badische Anilin- & Soda-Fabrik had to expend a million sterling on experiments and apparatus for the purpose.

As an example of research prosecuted to attain a definite end, not to prepare a compound already known, but by knowing the properties of compounds and the changes produced in these by changes in constitution, none is better fitted to illustrate the persistent and strenuous nature of the work of the highly-trained chemist than that involved in the discovery of salvarsan.

Dyes may be said to consist essentially of two distinct parts, to one of which the colour is due and to the other the power of fixing the colour on tissues. Many diseases are due to the life and the multiplication in the body of their host of multitudes of minute organisms termed protozoa, which in diseases such as sleeping sickness are known as "trypanosomes." Now Ehrlich found that the trypanosomes which he was investigating were always stained by

certain dyes which chemical research had proved to contain a definite grouping of atoms in their molecule. The idea struck him that he might kill these minute creatures by obtaining a compound which contained this fixative group of atoms, attached, not to a colour-giving group, but to one which would act as a poison to the protozoa. I need scarcely point out that a drug had to be discovered which, whilst it killed the germ, left the host unhurt. A series of such compounds was prepared in which the toxic element was arsenic. Each of these compounds had to be tested on the spirilla and on the higher living organism of the host by Ehrlich and his assistants. It was not until 605 unsuccessful compounds had been prepared and laboriously tested that "No. 606," or "salvarsan," the chemical name of which is dihydroxydiamino-arsenobenzene, was added to the list of successful drugs. Further research along similar lines has put even more efficient curative agents into the hands of the physician.

Just as we have the two types of research broadly marked out, so have we the two types of men who enlarge our knowledge; the one who feels that he can best fulfil his life's purpose by devoting himself to discovering new substances and new laws with the simple purpose of increasing the store of natural knowledge so that the man of the other type in due time may find uses for the substances and by means of the laws discovered apply them to the solution of problems in the arts and sciences. For the first the sole reward is too often the pure joy of having succeeded in his aim, realising fully that the successful applications of his discoveries and the money prizes attached to such will never be his. The public —even the enlightened portion of it—is too prone to regard at the time such original work as entirely useless. It is impressed infinitely more by the discovery of artificial indigo, of salvarsan, and of antipyrin, and the manufacturer agrees in this. The latter usually wants his research chemist (if he be so enlightened as to secure the services of one) to indicate his presence in the works by a visible increase on the income side of the balance sheet without any corresponding charge on the other side after, it may be, one or two or even three years' work, although he himself may, with a lifelong knowledge of the circumstances of his factory and its products, have been unable to effect this. In fact, it is by no means seldom that a research chemist at a miserable salary is only engaged in the same way that a specialist is often called in when the patient is on his deathbed, namely, as a last resort, whilst had his assistance been invoked at an earlier stage in the malady, it would have succeeded in achieving the desired effect. If the chemical manufacturer and those engaged in the allied industries are not only to hold their own, but to save themselves from an extinction as certain as the

death of every living organism, there is only one remedy, and that is to call in the services of the man who has been trained in the methods of advancing knowledge and whose education has been based on a sound acquaintance of the fundamental facts and theories of modern science. To keep along the same dead level of a fair measure of success is an existence which can only satisfy a decadent race and can only last for a very limited time. Our race has again shown itself in this War to be as full of energy, bravery, and chivalry as of old, but it is only gradually learning how much the neglect of research and the want of appreciation of a scientific training and education has cost it. Even our law-givers and law-makers are having the importance of scientific knowledge and training forced upon them, and perhaps no branch of science has had its utility more strikingly demonstrated for the time being than our own. But it has required hundreds of thousands of tons of T.N.T., lyddite, and dynamite to shake the foundations of their ignorance. When those of our defenders at the Front who have escaped the scientifically organised atrocities of our enemies and the consequences of the scientific ignorance of our rulers return home again we may venture to hope for the dawn of a new era in chemistry with perhaps brighter prospects of success than Boyle had two hundred years ago.

Our daily newspapers and our scientific journals have vied with one another in laying bare the various defects in our general and scientific education, organisation, and training so as to have left but little still unsaid.

It is evident that if the manufacturers are to employ properly trained chemists they must be provided with an adequate supply of men who not only know what is already known and may be merely walking cyclopædias, but men who have been trained to attack problems. The famous mathematical school of Cambridge which can point with pride to Newton, Stokes, Kelvin, Rayleigh, Thomson, and others, in its examinations makes a strong point of its "problem papers," in which neither the scientific nor even the cash value of the results are worth the paper on which the successful solutions are written. The training secured thereby is such as to enable those who are successful to tackle with every chance of success any problem which may present itself in after life.

Throughout my life I have been associated with educational matters, and these have always interested me profoundly, although I may not have bombarded the *Times* or its readers with my theories on the subject.

The son of the headmaster of a large grammar school in the south of Scotland, I went first to the University of Edinburgh and thence to Cambridge, and after nine years' residence there I left

to spend seven years in organising the science teaching in Durham School and Middlesbrough High School. Whilst there I had ample and unique opportunities of comparing the value of a classical with that of a scientific training from the purely educational viewpoint. After allowing fully for various social and other conditions at these two schools, I have no hesitation in recording as the result of my experience that the science subjects possess a much higher educational and more stimulating value than the classical subjects.

There are, however, many points which our newspaper correspondents who write so glibly on education overlook when throwing blame on the various educational authorities for their many shortcomings.

In the first place, the headmasters found it very hard indeed to obtain men who could really teach and keep order in a class of boys. To do this successfully meant that the science masters had been properly trained, and had such an intimate acquaintance with simple experimental methods that they did not require when showing, say, the union of hydrogen and oxygen in a eudiometer, to stand back as if they were afraid of being shot, and ignorant as to whether the eudiometer or the mercury, or perhaps both, were going to be distributed amongst the class. The teaching of chemistry was too often left to the junior mathematical master, who might also be asked to take the junior French class.

Again, in those schools which were fortunate enough to secure properly trained science masters, they were expected to prove their value to the school, not by sound, all-round fundamental teaching, but by devoting their spare time to the coaching up of the more promising of those boys who might be allowed to enter the despised "Modern Side" because they were not likely to gain a classical scholarship, but might possibly gain a scholarship in natural science. This, in turn, because of the many absurdly advanced questions set in the entrance and other scholarship examinations at the various Oxford and Cambridge Colleges, meant that candidates had to read and "get up" specialised branches of work of which at that stage they had better have been ignorant, devoting their energies instead to acquiring a sound knowledge of the principles and well-established experimental data underlying the various branches of science.

The evil does not end here, for if successful the newly-elected scholar is usually too proud to attend the so-called elementary lectures of the professor, which would do him all the good in the world, but pursues his course of attending advanced and special courses, becoming a specialist long before he ought to do so without having that broad base for his knowledge which is essential for true progress. His knowledge ought to be represented by the solidity of an Egyptian pyramid, instead of resembling a truncated cone

poised on its narrow end. Suitable as the latter type may be for the fellowship of a college, he is almost as unfitted as his fellow classic for active and useful life in an industrial centre and among industrial surroundings and problems.

The boy with brains at a public school who goes to Oxford or Cambridge, whose ambition is to lead the life of a student, devoting himself to intellectual pursuits in preference to going into any of the learned professions or into commerce of any kind, is taught to regard the Fellowship of a college as the first and most natural aim of his ambition. To obtain this his schoolmasters point out that the chances of his gaining such a prize are much greater if he studies classics, history, or mathematics, rather than any branch of natural science, even although the colleges may state that the opportunities for science students are just as great as for those in any other subject. This is not so, for the simple reason that the electors to the fellowships are in almost all colleges mainly classical men, who even if they wish to be strictly fair, as they undoubtedly do, cannot estimate the real value of what they are unable to understand. Hence the selection when made is too often a picturesque failure from the scientific point of view. Again, in some well-known cases with a powerful personality on the college council, all the fellowships which the college may devote to the encouragement of natural science are given exclusively to one branch of science, whilst other departments of science get none.

A concrete example will be more convincing and make my meaning more clear than any number of general assertions. I have therefore compiled the following analysis from the Natural Sciences Tripos lists as given in the Cambridge University Calendar for 1915–1916. These lists are now given for the last ten years only, but are sufficient to prove my point.

These ten lists contain the names of 122 candidates who have gained First Class Honours in Part II. of the Tripos, and are arranged under the following subjects:

	First Class Honours.	Fellowships.
Physics	32	7
Chemistry	31	0
Mineralogy	1	0
Geology	11	2
Botany	13	1
Physiology	21	4
Zoology	11	3
Anatomy	2	0
Total	122	17

That is to say, that of the seventeen Fellowships devoted to the encouragement of natural science *not one* has been given for proficiency in Chemistry, whilst no fewer than seven have been

allotted to Physics with practically the same number of successful candidates. Are the chemists so inferior intellectually to all the other candidates as this would seem to indicate, or what is the explanation of this preposterous state of affairs?

Nor is it only the younger chemists who suffer in this way, for even University Lecturers in Chemistry may devote forty years to teaching and the encouragement of research amongst their pupils and be themselves Fellows of the Royal Society without being elected to a College Fellowship.

Let us suppose the brilliant schoolboy selects chemistry as his subject, and gains a scholarship, and takes all the honours possible in his college and university examinations, what is the prospect before him? He *may* be elected to a fellowship, and be content to settle down to the pleasant life of the university and do his share in its teaching for what can only be regarded as a mere pittance. He may give up that and go to the Bar, where he may do fairly well now that scientific knowledge has some value, as disputes on patent and other subjects depending on chemistry are more frequent than they used to be. There is no prize held up before him, such as, say, a bishopric, no chance of his becoming a Cabinet Minister or the holder of any high office in the State, because he has proved himself to be a first-rate scientific man. At present any such proof seems to mark him out as unfit, instead of being regarded as a special qualification.

What opening is put before him in chemical industry? What salaries or wages are offered to tempt anyone with brains above the average to direct his studies or research work with a view to preparing himself for any work relating to chemical manufactures? When the manufacturers learn to appreciate the value of men thoroughly trained in research work they will find the universities and technical colleges amply fitted to train the men for them, and more than willing to do everything in their power to assist them; but if they want a good article they must be prepared to pay for it.

The examinations for the Civil Service, whether at home or abroad, are all heavily weighted in favour of the classical and mathematical candidates. Everything which is calculated to test a man's ability to tackle an unknown problem, however simple in its nature, is carefully excluded by a cautiously worded syllabus which details the range of the facts and the nature of the tests which may be applied.

Surely it is time to change this state of affairs!

OBITUARY NOTICES.

JOHN LLEWELYN DAVIES.

BORN SEPTEMBER 10TH, 1879; DIED OF WOUNDS, SEPTEMBER 26TH, 1915.

MAJOR JOHN LLEWELYN DAVIES, who died in hospital at Wesel from wounds received near Loos-Hulluch on September 25th–26th, was the son of Mr. and Mrs. D. J. Davies, of Neath. Born in September, 1879, he was educated at Ald. Davies's School (where his father was headmaster), University College, Aberystwyth, and at Emmanuel College, Cambridge, where he obtained a 1st Class in Part I. of his Tripos and a 2nd Class in Part II. On leaving Cambridge, Major Davies went as lecturer to Carmarthen Training College for a short period, and subsequently became science master at the Perse School, Cambridge. In May, 1915, he was appointed headmaster of Cardiff High School, a deputy filling the position during his absence on military duties.

As a schoolmaster, Major Davies was thorough and successful, enjoying great popularity among his boys and colleagues. His pupils gained many open scholarships at the universities.

Soon after the outbreak of war, Major Davies obtained a Captaincy in the 11th Essex Regiment, and was promoted Major last June.

JAMES LOUIS FOUCAR.

BORN OCTOBER 15TH, 1882; KILLED IN ACTION, MAY 8TH, 1915.

MAJOR JAMES LOUIS FOUCAR, B.Sc., aged thirty-two, was educated at the Blackheath School, afterwards taking his degree with honours at the University of London.

His scientific attainments were fully recognised in the various learned societies with which he was associated, and he was ever ready to benefit others in the interests of scientific education by his own practical experience, which comprised so great a variety of subjects. He was engaged in scientific research in Italy when war was declared against Germany, but immediately returned to rejoin his regiment, "The Rangers," T.F., and in a few months was ordered to the Front, where he served during most of the sharpest

engagements. On May 8th, after the second battle of Ypres, he was reported missing, then believed killed, all the other officers being either killed, wounded, or missing.

IVAN RICHARD GIBBS.

Born July 6th, 1891; Killed in Action, September 25th, 1915.

Captain Ivan Richard Gibbs, who was killed in action at Loos on September 25th, 1915, was the son of Mr. and Mrs. W. H. Gibbs, of 22 Montpellier Villas, Cheltenham, and was twenty-four years of age.

Educated at Cheltenham Grammar School, he was elected to an Open Exhibition in Natural Science at Jesus College, Oxford, in 1910, and graduated three years later. As an undergraduate he was an active organiser of the College athletics, and an enthusiastic member of the O.U.O.T.C. Before volunteering for active service at the commencement of the war he had been acting as Assistant Demonstrator in Chemistry at the Imperial College, South Kensington, and there, as at Oxford, won the affection and high esteem of the staff and students.

In collaboration with T. W. Robertson he completed in 1914 a research on the migration of para-halogen atoms in phenols, which has been published in the *Transactions*.

D. L. Chapman.

FRANK STEVENSON LONG.

Killed in Action, September 26th, 1915.

Lieutenant Frank Stevenson Long, 11th Essex Regiment, who was at first reported wounded and missing, was afterwards stated to have been killed in action about September 26th. He was educated at Parmiter's Foundation School, Bethnal Green (1898–1906), and while here he showed a distinct bent for science. During his last year he was captain of the school. On leaving he was awarded a Drapers' Company's Scholarship, which he held at East London College.

In 1909 he obtained his B.Sc. with 1st Class Honours in chemistry. He then became a demonstrator in the Chemical Department, and was engaged in teaching and research work. While holding this post he turned his attention also to physics, and in 1911 obtained 2nd Class Honours in the B.Sc. Examination. He

was elected a Fellow of the Chemical Society in 1911, and the results of some of his work are recorded in the *Transactions*.

He then proceeded to Cambridge as a student in the Secondary Department of the Day Training College for Teachers. Later he was attached to Fitzwilliam Hall, being at first Secretary to the Censor and afterwards to the Librarian.

He gained a first class in the Mathematical Tripos Pt. I. in June, 1914, and was looking forward to taking Physics in 1915.

He had been a member of the London University O.T.C. for three years, and for two years a member of the Cambridge University O.T.C.

He obtained his commission in September, 1914.

In announcing Long's death at the meeting of the Chemical Society on December 2nd, 1915, the President remarked that the Society had lost "one of the best type of Fellows, well qualified in chemistry and physics, and with a competent knowledge of mathematics."

His bearing was as modest as it was engaging, and as a consequence of this he was held dear by all who knew him.

No one could have thrown himself with greater zest into the social life of his schools and colleges, and many a fellow student owes to his influence an outlook towards higher things. He was a thorough sportsman, keen on football and rowing.

While recognising that he gave his life in a noble cause, one cannot but deplore the early close of a life which in many directions, not least in scientific channels, was so full of promise.

S. H. Woolhouse.

RICHARD ARNOLD SEYMOUR-JONES.

Born May 18th, 1889; Killed in Action, March 27th, 1915.

Richard Arnold Seymour-Jones, who was killed in action on March 27th, 1915, in his twenty-sixth year, was elected a Fellow of the Society in 1912. He was born at Wrexham on May 18th, 1889, and was educated at Wellington College (Salop), thence matriculating at the Leeds University. Here he studied applied chemistry, graduating as Bachelor of Science with first class honours in the chemistry of leather manufacture in 1910, being awarded also the Le Blanc medal for special distinction. He took his M.Sc. the following year, being meanwhile engaged as research assistant to Professor Procter during his work on the acid swelling of gelatin at the University. He did much valuable work on the little-known chemistry of tanning, dealing especially with the questions of the

acids present in tan liquors, the estimation of mercuric salts at great dilutions, and the chemistry of skin. The results of his work are embodied in various papers read before the Society of Chemical Industry.

In 1912 he moved to Warrington, taking charge of a department of technical scientific research at Messrs. Joseph Crosfield and Sons, Ltd. Here he was mainly engaged in the important applications of physical and colloidal chemistry to the soap industry, work which naturally cannot be published.

He was a keen sportsman, being prominent at Leeds at hockey, boxing, swimming, and cricket. In 1911 he was awarded the Royal Humane Society's certificate for a gallant attempt to save a woman from drowning.

A Territorial officer for several years prior to the war, he proceeded to France with his battalion in February, 1915, and met his death in the trenches the following month.

His was a mind ever fertile with new ideas, and he possessed the ability to carry them out easily. Although mainly engaged in the practical applications of chemistry, at Leeds he did much work which at the time promised to be of only academic interest, work which later he was able to utilise in application to problems in the soap industry.

ROBERT JOHN CALDWELL.

DIED, APRIL 4TH, 1915.

ROBERT JOHN CALDWELL was educated at the Aske's School, Hatcham. He entered the City and Guilds' College, Kensington, in 1901 as Clothworkers' Scholar; having gained the first place in the entrance examination he was sufficiently advanced to join the second year's course.

He was awarded the Diploma of A.C.G.I. in 1903; in the following year he was elected to the Leathersellers' Company's Research Fellowship, and held this for three years. In 1907 he was awarded the D.Sc. (London) for chemical research. Caldwell's first inquiries were carried out jointly with the writer on the saccharoclastic action of acids as contrasted with that of enzymes (*Proc. Roy. Soc.*, 1904, **73**, 526) and on the hydrolysis of cane sugar by very dilute acids (*ibid.*, **74**, 195). In the first paper put forward, the "active system" theory of hydrolysis propounded for enzyme action was applied to acids and shown not to be at variance with any of the

known facts, whereas the alternative ionic explanation was beset with difficulties. In the later paper it was argued that when hydrolysis was effected by sufficiently dilute acids the course of the change approximated during the earlier period to a linear function of the time. In the course of this work the experimental method was carefully elaborated so as to give the most delicate measurements of hydrolysis obtained to that date, but he greatly improved on these in the course of his subsequent work.

In 1912, when still greater accuracy in measurement was possible, the work with very dilute acids was repeated by Worley (*Proc. Roy. Soc.*, [*A*], **87**, 555), who showed that whilst Caldwell's experiments were sound, the interpretation put upon them was open to question on the ground of the mathematical treatment adopted.

Subsequently the apparatus which had been set up was utilised by Caldwell to compare the hydrolytic activity of two isomeric acids of opposite activity, namely, *d*- and *l*-camphorsulphonic acids, but no evidence of a difference in their activity could be obtained (*ibid.*, **74**, 184).

He presented an exhaustive and most valuable report on the hydrolysis of sugars to the British Association at the York meeting in 1906, which was printed *in extenso*. As Leathersellers' Fellow (under the guidance of Professor H. E. Armstrong) he began the long series of "Studies of the Processes operative in Solutions," which have been published from the Central Technical College. His contributions are entitled, "The sucroclastic action of acids as influenced by salts and non-electrolytes" (*Proc. Roy. Soc.*, 1906, [*A*], **78**, 272); "The discrimination of hydrates in solution" (*ibid.*, 1907, [*A*], **79**, 586); "The changes affected by the reciprocal interferences of cane sugar and other substances in aqueous solutions" (*ibid.*, 1908, [*A*], **81**, 117).

Having then decided to follow a technical career, he became chemist and manager to the Pfleumatic Syndicate, Ltd. This company was engaged in the development of solid motor tyres filled with a composition made from gelatin; Caldwell worked first in London and afterwards in Southampton at the works of Messrs. Harland and Wolff. Subsequently in 1912 he was entrusted by this firm with the establishment of a scientific department at their Belfast works. He died from pneumonia after a very short illness on April 4th, 1915.

Caldwell was a man of exceptional ability. He had an extensive knowledge of his subject, well-developed critical faculties, and great power of application and industry. He was one of the most promising and able of the younger technical chemists, and his early death is a great loss to industry.

He was a keen member of the Electrical Engineer Volunteers, and did much for the various college societies in his student days.

E. F. A.

SIR ARTHUR HERBERT CHURCH, K.C.V.O.

BORN, JUNE 2ND, 1834; DIED, MAY 31ST, 1915.

SIR ARTHUR HERBERT CHURCH seems to have been a descendant of an old Essex family of the name of Church, one of whom was Groom of the Privy Chamber, and afterwards Equerry to the Queen of Charles the First. His immediate ancestors held various posts in connexion with the Government, and he was also connected by marriage, through his ancestry, with Benjamin Booty, of Walsingham, County Norfolk. Sir Arthur Church's own father, after serving for a short time as a midshipman under his uncle, Captain Church, reliquished the sea for the law, and married his second cousin, Maria Susannah Booty, on October 17th, 1817. His father held various legal appointments, and died on November 18th, 1858, in his seventy-first year.

Sir Arthur Herbert Church was born on June 2nd, 1834. He married on May 3rd, 1879, in the Parish Church of Leeds, Jemima, third and youngest daughter of the late John Buckingham Pope. The varied interests which Sir Arthur Church showed during his life, his wide culture and knowledge of other departments of learning in addition to his special line of chemistry, are no doubt to be traced to this long descent through an ancestry who were not only people of some position, but also people of culture and education, as is shown by the various posts they held in their lifetime and the duties they fulfilled.

Sir Arthur Church began his school days at a preparatory school in Brighton, kept by an Englishwoman who was married to a German of the name of Reinecke. On account of our recent experiences of the German nation, it is interesting to hear that he was very unhappy at this school because of the harsh and unsympathetic treatment he received. Afterwards he went to King's College School in London, and from there he came back to another private school at Brighton, where he seems to have found a lifelong friend in one of the assistant masters, John Eyre Ashby, whilst he received his first lessons in drawing and painting from Mr. Ley. It is interesting to note that in those early days some encouragement was given at the Brighton school to the study of natural science, a kind of workshop being provided, where some of Sir Arthur Church's first chemical experiments were made. In the year 1851

he left the school in Brighton for the Royal College of Chemistry in Oxford Street, where he had the fortune for so young a lad of coming into contact with many brilliant chemists. At that time A. W. Hofmann was the professor, C. L. Bloxam, F. A. Abel, William Crookes, John Spiller, and A. B. Northcote were among the demonstrators, whilst working at an adjoining bench was W. H. Perkin. Others who were to become in after-life well-known chemists were among his fellow students, and it is of great interest to note how many celebrated men who have contributed so much to the development of chemical science came from the laboratory in Oxford Street in those early days. Sir Arthur Church continued as an assistant in the professor's private laboratory there, carrying out researches, and during that time he met both Faraday and Tyndall.

At this time he seems to have been hesitating between the career of a man of science and that of an artist. Tyndall published in the *Philosophical Magazine* a letter which Sir Arthur Church had addressed to him on the suspension of chemical action in the case of bodies in the spheroidal state, in the year 1854—a year in which a picture painted by Sir Arthur Church appeared in the May Exhibition of the Royal Academy. Although the attractions of science ultimately proved stronger than those of art, and painting became a holiday recreation, he continued to exhibit and even to sell pictures at the Royal Academy and the British Institution.

On June 29th, 1855, he received his testimonial of proficiency, which was signed and autographed by Prince Albert, as well as by Dr. Hofmann. He then went to Oxford, where he became a research assistant to Sir B. C. Brodie, the Professor of Chemistry, and it was there that the experiments he was carrying out for the professor on graphite resulted in the discovery of that interesting compound known as graphitic acid. On November 13th, 1856, he matriculated from Lincoln College, and while studying for his degree published, in collaboration with A. B. Northcote, a manual of qualitative chemical analysis. Ultimately he graduated with honours in the natural science school. He then opened a laboratory in London as a consulting chemist and chemical tutor.

In 1863, on the resignation by Dr. Voelcker from the Professorship of Chemistry in the Royal Agricultural College at Cirencester, he was appointed to succeed him. This professorship he held for nearly sixteen years, during which time he published his "Laboratory Guide: a Manual of Practical Chemistry," and two other books, one on "Colour" and the other on "Food," as well as a large number of researches.

Owing to the varied departments of chemistry in which Sir

Arthur Church did original work it is very difficult to select from amongst his published researches those which are of the greatest interest. A considerable number of his papers deal with organic chemistry, many of which were published in the *Philosophical Magazine*, whilst his work in the department of mineral chemistry is of great importance, and more especially occupied him during his time at Cirencester. While there, he was naturally drawn into the study of problems connected with agriculture, and in addition he published some interesting researches on the use of the micro-spectroscope, these researches leading him, I believe, ultimately to become a recognised expert on gems and precious stones, the micro-spectroscopic phenomena of which he had thoroughly investigated. During his researches at Cirencester he added to the list of known British minerals, one which, after his own name, is called churchite; but perhaps the most curious and interesting of his researches at this time was that into the remarkable bird-pigment, containing 7 per cent. of copper, and known as turacin. His agricultural investigations led him into an inquiry into the chemistry of plants, resulting in papers on the occurrence of aluminium in some vascular cryptogams; the composition and properties of colein or erythrophyll; the chemical study of vegetable albinism; the invention of the "lithium-method" for the study of certain problems in plant-life; and a method of estimating albuminoid nitrogen in roots and other vegetable food-stuffs. The amount of work during these years must have been enormous, as scores of analyses were made of many insufficiently studied mineral species, and it was here that he first began to be interested in chemistry as applied to archæological research. Cirencester has always been celebrated for its Roman remains, and it possesses a most interesting museum of Roman antiquities, founded by the Earl of Bathurst. This led to his investigating antique glass, Roman coins, and other metal work, and at this time he seems also to have become interested in the collection of china, which induced him to make a chemical inquiry into Oriental and English porcelains. Throughout his life he was a great collector, and during these years he acted as curator of this Cirencester museum of Roman antiquities, and published a guide-book to the museum. In 1879, on his marriage, he resigned his professorship at Cirencester, and settled in London, ultimately building "Shelsley," close to Kew Gardens, a delightful house, full of valuable collections, not only of pictures, but also of Oriental bronzes, porcelain, antique embroideries, English pottery, and a unique collection of Japanese sword-guards.

Every one of these æsthetic and artistic interests of Sir Arthur Church proved to be of value in the development of applied science,

as in any direction in which he became a collector he also became an investigator into the chemistry and the manufacture of the various articles in which he was interested.

In 1879 he was appointed Professor of Chemistry at the Royal Academy, and by this appointment his attention was directed more thoroughly than before to the chemistry of painting and the study, not only of the best conditions for obtaining permanent pigments and vehicles for modern work, but also the study of the whole early history of painting, and the methods so successfully used by the old artists for producing durable work. The close connexion between his scientific and æsthetic interests is shown by the fact that he gave a course of Cantor lectures at the Society of Arts on the points of contact between scientific and artistic aspects of pottery during this time, and acted as juror in several of the International Exhibitions at South Kensington. He also undertook the cleaning and restoring of some Italian tempera-portraits on panel, the work of Bartolomeo Suardi; whilst in 1883 he published his "Handbook of Precious Stones" for the Science and Art Department, and gave a special course of lectures at South Kensington Museum on the chemistry of paints and painting.

During this time he was still engaged in agricultural chemistry, lecturing at the Downton College of Agriculture, and at Bedford College, London, and he published in 1886 a South Kensington handbook on The Food-grains of India. In 1890 he published his "Chemistry of Paints and Painting," which has now run through several editions, and is the standard work on this subject. In 1898 he was appointed President of the Mineralogical Society, in succession to Mr. Story Maskelyne.

One of the most interesting pieces of work which he undertook during his later years was the examination and preservation of the Westminster frescoes. On the building of the new Houses of Parliament, well-known English artists, including Maclise, Cope, Dyce, Herbert, and Ward, had been entrusted with the painting of frescoes, an attempt being made to revive some of the older methods and also to test certain newer methods for fresco painting. These frescoes had unfortunately rapidly deteriorated, and their examination and preservation were put into the hands of Sir Arthur Church. His reports in four Parliamentary papers on the wall-paintings in Westminster Palace are of great interest [Cd. 7651 (1895), Cd. 8054 (1896), Cd. 8893 (1898), and Cd. 3085 (1906)].

The last piece of work which was done by Sir Arthur Church was a very careful catalogue which he prepared for the Royal Society of early documents in the Society's possession, covering the period from 1741 to 1806—a most valuable piece of work, and

most useful catalogue of reference. It is impossible to give here a list of the innumerable papers published by him in the different departments of science in which he worked, but the following are the titles of the books which he published, having a bearing both on science and art, and the applied industries in which the two are closely interwoven:

"The Laboratory Guide," first published in 1864. 8th edition, 1904.

"Food." This handbook is now, it is believed, out of print.

"Precious Stones," a museum handbook of the Board of Education; first published, 1882; revised edition, 1908.

"English Earthenware," a museum handbook; first published 1884, and since several times revised.

"English Porcelain." First published in 1885; last issue, 1904.

"Corinium Museum Guide." The 9th edition of this pamphlet appeared in 1905.

"The Chemistry of Paints and Painting," the latest edition of which appeared in 1914.

"Josiah Wedgwood." Monograph; first published in 1894; new and revised edition, 1903.

"The Conservation of Historic Buildings and Frescoes." A lecture delivered at the Royal Institution in 1907, and published in volume 18 of the *Proceedings*. This is a summary of his work in the conservation of urban stone-work and wall-paintings.

He also published three papers by John Evelyn, which he discovered among the uncatalogued manuscripts of the Royal Society. These were: Evelyn's "Sculptura," "Arts Illiberal and Mechanick," and "A Designe for a Library."

To sum up the work that has been done by Sir Arthur Church and its value is an almost impossible task on account of the varied interests both in science and in art with which his mind was occupied, but some attempt has been made to indicate these in the course of this short account of his career.

Sir Arthur Church occupied a unique place among men of science. There are, and have been, of course, men of science who outside their laboratories were also men of culture and interested in other departments of thought, but Sir Arthur Church made peculiarly his own a department of chemistry which has seldom attracted the pure chemist—although he had a precursor in Sir Humphry Davy—a department in which science and art are found as handmaidens in the production of works of art. In the great artistic periods of the past various technical discoveries were made, and there was wonderful progress in the study of practical chemistry, without an understanding of the processes upon which it

depended. In the modern scientific period great progress has been made in the application of science to technical processes—a progress which has usually resulted in turning out large quantities of cheap articles with the complete sacrifice of any artistic merit whatever.

During the latter half of the nineteenth century the essential inferiority of modern technical processes was begun to be realised, and attempts were being made on the part of men of artistic training—of whom William Morris was the leader—to study minutely the technical processes of the past, and to combine artistic merit and design with fine technical production. There was also a realisation on the part of students of history and archæology that when the political history of a period had been written there remained a large amount of material of great interest, dealing with the way in which people actually lived, and their processes and methods of making articles of use and artistic merit, whilst there was a growing reverence for the skill and ingenuity of our ancestors, and a realisation that we had lost much in the development of modern mechanical processes. Of this movement, which is still going on, and is slowly and dimly feeling its way to a different standard of workmanship, and therefore a different standard of life for those engaged in the crafts, Sir Arthur Church may be described as the man of science. His intense appreciation of artistic work of all kinds, his enthusiasm as a collector, and his profound interest in archæology, led him to apply modern scientific methods to solving the technical problems of the past, and combining in the most interesting way the study of art for art's sake, with the application to it of chemistry.

Whilst, therefore, the work of Sir Arthur Church in many departments of pure science has added many bricks to the structure of modern chemistry, it is probably in this direction that he will best be remembered, in which he has placed a unique mark on the history of science in the nineteenth century.

Science is only too closely associated in the minds both of scholars and artists with a somewhat crude and modern vandalism. Sir Arthur Church did much to retrieve it from that position, and to give it its true place among the departments of "polite learning." A complete list of Sir Arthur Church's researches and papers up to 1909 will be found in a private memoir, "Records and Recollections," which he himself wrote and dedicated to his wife.

A. P. Laurie.

TAMEMASA HAGA.

BORN MAY 23RD, 1856; DIED NOVEMBER 21ST, 1914.

TAMEMASA HAGA was born in Tokyo on May 23rd, 1856. His father, who was a *samurai*, was also a scholar in Chinese classics, and the education which Haga received in his early boyhood was, naturally, for the most part literary. When, however, after the Restoration of 1867 Western sciences were systematically introduced into Japan and their cultivation encouraged by the Government, Haga chose to enter the Engineering College newly established at Toranomon. Here he studied chemistry under the late Dr. Edward Divers, and, deeply impressed by the personality and example of his teacher, Haga early imbibed that spirit of experimental research which pervaded throughout his future career, and made him one of the foremost chemists of his country. On graduating from the Engineering College in 1881, Haga was at once made one of Dr. Divers's private assistants, with promotion some years later to an assistant professorship, and when the Engineering College was amalgamated with the Imperial University in 1886, both his and Divers's services were transferred to the College of Science.

In the latter institution, as in the Engineering College, Haga proved himself an untiring and devoted cultivator of science, and Divers, who found in him a most able and trustworthy collaborator, was fully aware of the fact that without this collaborator he could not have done one-half of what he actually effected. In 1899, when Divers retired and left Japan, Haga was promoted to the full professorship as his successor, and occupied the chair of inorganic chemistry. For the next ten years both his energy and his devotion to science never abated in the least, but in the winter of 1909 symptoms of lung disease became apparent in him, and ever afterward he was obliged to live much in the country. Haga ultimately retired in 1913, abandoning his work altogether, and in the next year—on November 21st, 1914—he passed away at the age of fifty-eight, leaving his wife and three children to mourn him. He was simple in manners, refined in taste, and utterly indifferent to worldly ambitions.

Haga obtained the degree of Doctor of Science (Tokyo) in 1894, and on his resignation the University honoured him with the title of Emeritus Professor. The Government also recognised his merit, and bestowed on him the decoration of the Sacred Treasure of the Third Order. He was elected a member of the Tokyo Chemical Society in 1884, of which he was president in 1908–1909. The

Chemical Society of London elected him a Fellow in 1886. He was also a member of the Chemical Society of Berlin.

Haga's scientific activity extended for a period of nearly thirty years, during which he published no fewer than twenty-eight papers in the *Journal of the Chemical Society*, for the greater part jointly with Divers. The most important of these are those on that group of numerous and complex acids and their salts, the so-called sulphonated nitrogen compounds, which were first studied by Frémy, and later by Berglund, Claus, Raschig, and others, but were for the first time thoroughly and systematically investigated by Divers and Haga. These two chemists showed that in spite of the apparent complexity of these compounds they may all be produced by the reaction between nitrous and sulphurous acids, the primary product of this reaction being always hydroxylaminedisulphonic acid, $HON(SO_3H)_2$, from which all the others may be either directly or indirectly obtained. Besides establishing this general conclusion of great importance, and thereby rendering the chemistry of these compounds comparatively simple, they minutely studied the properties of amidosulphonic acid, $H_2N{\cdot}SO_3H$, oxyamidosulphonic acid, $HO{\cdot}NH{\cdot}SO_3H$, imidosulphonic acid, $HN(SO_3H)_2$, oximidosulphonic acid, $HON(SO_3H)_2$, nitrilosulphuric acid, $N(SO_3H)_3$, and several other like acids, preparing and describing at the same time a large number of the salts of these acids.

Haga's independent contributions to our knowledge of the same group of compounds are contained in the papers on peroxylaminesulphonates and hydroxylaminetrisulphonates (T., 1904, **85**, 78), hydroxylamine-$\alpha\beta$-disulphonates (T., 1906, **89**, 240), and a simple method of preparing the imides of the sulphonic acids (*J. Coll. Sci. Tokyo*, **25**, Art. 13), in all of which there is an abundant proof that the author possessed in a high degree those qualities which are essential for a successful investigator, namely, keenness of insight and dexterity in experimentation. This is especially true of his work on peroxylaminesulphonates, unusually unstable compounds, the preparation and analysis of which present more than ordinary difficulties.

Inorganic chemistry was not the only field in which Haga interested himself, for while in Germany (1896–1898) he was chiefly occupied with the investigation of organic compounds containing nitrogen, and jointly with Harries he published three papers on these compounds (*Ber.*, 1898, **31**, 56, 550; 1899, **32**, 1191), besides publishing, at a later date and in collaboration with one of his own students, a paper on the anhydro-bases of the fatty diamines (*Ber.*, 1903, **36**, 333).

In concluding this short notice of the life and work of Tamemasa Haga the writer cannot refrain from observing that although collaboration in scientific work is quite a common thing, it will be difficult to cite a case where this collaboration was more complete than was that of Divers and Haga. Their association in scientific work extended for nearly twenty years, and except for a short interruption of about two years, while Haga was abroad, these two men worked together from morn until night, both with untiring exertion and undivided devotion to science, and mutually and completely loving and respecting one another.

JOJI SAKURAI.

VIVIAN BYAM LEWES.

BORN, 1852; DIED, OCTOBER 23RD, 1915.

VIVIAN BYAM LEWES died at Mold, Flintshire, on October 23rd, 1915, having gone to that town five days previously to deliver a lecture on "The Explosives used in the Great War." Although far from well, he determined to fulfil his engagement, for he always made a strong point of not disappointing an audience, but on arrival at Mold he was in a state of collapse and pneumonia rapidly developed. His death preceded by a few weeks only that of his old chief and valued friend, Professor H. Debus.

Lewes was born in 1852, and, owing to the death of his father, his uncle, George Henry Lewes, the well-known author of the "History of Philosophy," assumed responsibility for his education. On leaving University College School he became assistant to Dr. F. S. Barff, and in 1870 to Professor A. W. Williamson at University College. Later he was in charge of the Birkbeck laboratories under Dr. C. Graham. In 1879 he was appointed assistant in the chemical department of the Royal Naval College, Greenwich, succeeding Dr. Debus as Professor of Chemistry in 1888, a post from which he retired in October, 1914. He was elected a Fellow of the Society in March, 1888. During his long association of thirty-five years with the senior service, Lewes's ability as a lecturer, and his genial personality, gained him the friendship and esteem of a large circle of naval officers. Numerous problems associated with the navy necessarily came before him for investigation, and he served on Admiralty committees on anti-fouling compositions and oil fuel. At the time of his death he was Chairman of the Chemical Section of the Munitions Inventions panel.

He was a vice-president of the Institution of Naval Architects, and this body awarded him its first gold medal for a paper on

"The Formation of Boiler Incrustations and Oily Deposits." He contributed other important papers on the corrosion of metals, anti-fouling compositions, and the spontaneous ignition of coal.

His chief scientific work was in connexion with the cause of luminosity of hydrocarbon flames. In 1892 he communicated to the Chemical Society a paper on "The Luminosity of Coal Gas Flames" (T., 1892, **61**, 322), which was subjected to considerable criticism by Prof. Smithells (T., 1895, **67**, 1049). Lewes replied in a further contribution, "The Acetylene Theory of Luminosity" (T., 1896, **69**, 226), claiming that the acetylene theory was supported by the following facts: (1) that the largest proportion of the unsaturated hydrocarbons in a gas flame is converted into acetylene before luminosity commences; (2) that acetylene develops luminosity when heated to a temperature at which it decomposes, the conditions under which this takes place rendering the presence of atmospheric oxygen impossible; (3) that the temperature necessary to decompose acetylene with luminosity is insufficient to raise the carbon liberated from it to the point at which it emits light (the heat developed by the exothermic decomposition of the acetylene raising the liberated carbon particles to a state of incandescence); (4) that in luminous hydrocarbon flames of sufficiently high temperature the luminosity varies directly with the amount of acetylene present when luminosity commences. In the *Proceedings of the Royal Society* Lewes published two papers on the action of heat on ethylene (1894, **55**, 90; 1895, **57**, 394), and another paper on "The Cause of Luminosity of Hydrocarbon Gases" (1895, **57**, 450). His earliest papers before the Chemical Society were on pentathionic acid (T., 1881, **39**, 68) and tetra- and penta-thionate of potassium (T., 1893, **41**, 300), and later, with R. Cowper, a paper on "The Oxidation of Phosphorus at a Low Temperature and the Alleged Decomposition of Phosphorus Anhydride by Sunlight" (T., 1884, **45**, 10).

Professor Lewes's principal sphere of activity was in connexion with coal gas, his interest in this direction doubtless arising from his early association with Williamson, who was Chief Gas Examiner. Lewes was appointed as assistant Gas Examiner to the Corporation of the City of London in 1880, and became Chief Gas Examiner in 1892, an office which he filled at the time of his death. In connexion with coal gas he contributed a large number of papers to the various technical societies; he was always a welcome lecturer before the Institution of Gas Engineers, of which body he was elected an honorary member in 1903. In litigation and Parliamentary business connected with the industry Lewes always was called upon as an expert witness, his gift of repartee constituting

him a witness with whom opposing counsel had to deal circumspectly.

Lewes was an ideal public lecturer, having the rare gift of being able to treat a scientific subject in a popular manner easily followed by his audience. No lecturer was more welcome on the platform of the Royal Society of Arts; here he easily held the record with more than sixty lectures. In all he delivered nine series of Cantor Lectures, the majority in connexion with coal gas and its applications; others were on explosives and their development (1904), and acetylene (1898). For many years he delivered lectures throughout the country under the Gilchrist Trust, being associated in this work with such able lecturers as Sir Robert Ball and Dr. Dallinger. As a lecturer under the University Extension scheme he did excellent pioneer work, and undoubtedly contributed to the success of many of our technical institutes, for the number of students induced to follow up their preliminary work at Lewes's lectures by systematic study was indeed large. Certainly no chemist has been more successful in imparting to others a desire for further study of his subject than Lewes.

He was closely associated with the introduction of acetylene gas and its development in this country. In 1892 Willson first obtained calcium carbide on a commercial scale, and at a lecture at the Royal Society of Arts Lewes first brought this material, and the possibilities of acetylene generated from it, to the notice of an English audience. He was quick to realise the importance of the new material, and contributed largely to the development of the industry which followed in the train of its commercial discovery. His quick insight led in one or two instances to his becoming an enthusiastic advocate of processes which have not, up to the present, developed as he hoped, but which are likely to attain the importance he anticipated at no very distant date; for example, the distillation of coal at a low temperature and the use of blue water-gas introduced into the retorts during the distillation of coal for illuminating gas.

Professor Lewes, in addition to the large number of papers and lectures contributed to various technical journals, was the author of several books. His large volume on acetylene is a standard work. Other text-books include "Service Chemistry," "The Carbonisation of Coal," and "Liquid and Gaseous Fuel."

Lewes was a man of charming personality and genial presence, kindly and generous in the extreme. His was the cheerful soul, ever ready with an apt repartee; ever ready with a timely jest. No more lovable man ever breathed. In one appreciative memoir we find: "It is said that no man is irreplaceable, but if any man

ever stood astride this proverbial saying, that man was Professor Lewes."

J. S. S. B.

DAVID ALEXANDER LOUIS.

BORN, 1856; DIED, MARCH 25TH, 1915.

DAVID ALEXANDER LOUIS, who died on March 25th, 1915, in his fifty-ninth year, was elected a Fellow of the Chemical Society in 1878. Between 1876 and 1881 he passed through the mining and metallurgical and part of the chemical and other courses at the Royal School of Mines, after leaving which, his work was of an extremely varied nature both in the early days and throughout his career. Owing to his great versatility, his Bohemian habits, and his independent means, he never devoted himself to any special branch of science, and it would be difficult to say whether he could best be described as a mining man, metallurgist, chemist, or journalist. Much of his early work consisted in lecturing and contributing to the technical Press but, at the commencement of his career, he was also engaged at the Sir John Lawes Agricultural Experimental Station, at dye-works, etc., in mining in Cornwall, and in metallurgical work in various parts of the United Kingdom. Later, he travelled on mining and metallurgical business in Colorado, Montana, Germany, Austria, Italy, France, Hungary, Russia, Sweden, Norway, Bohemia, the Caucasus, Persia, Galicia, the Balkan States, Rumania, Egypt, Siberia, and the Far East.

Most of his work was connected with metalliferous minerals, but a considerable amount of his attention during later years was devoted to coal and coke and to the petroleum industry. He was lecturer on mining at the Yorkshire College of Leeds for a short period, and was for many years lecturer on mining at the Crystal Palace School of Practical Engineering, and one of the Assistant Examiners in Mining to the Board of Education. He contributed numerous papers to the Chemical Society, the Institution of Mining and Metallurgy, the Iron and Steel Institute, and other technical and learned societies, and was well known as a contributor to the technical Press. He was joint author with Sir Edward Frankland of two papers read in 1880 on the "Action of Zinc Ethyl on Azobenzene" and the "Action of Zinc Ethyl on Benzoylic Cyanide" respectively, and, with Sir Boverton Redwood, of the section on miners' safety lamps, in Groves and Thorpe's "Chemical Technology."

Louis was one of the most familiar attendants at the meetings and excursions held by the British Association, the Geologist's

Association, the Iron and Steel Institute, and the Society of Chemical Industry. He was an outspoken critic, both verbally and in writing, and his wide knowledge and experience of technical work and of men, enabled him to regard scientific and technical questions from the broadest point of view, so that, although his criticisms were destructive rather than constructive, they were none the less fruitful.

He was extremely active in connexion with the social side of our meetings and with the organisation of many movements. For some years he was Secretary to the Royal School of Mines dinner; he carried out the bulk of the work in connexion with the Wingham Benevolent Fund, and was the secretary or one of the leading spirits at many meetings of journalists and scientific men, whose excursions owed much to his organising ability and personality. He was the Honorary Secretary of the Mining and Metallurgical Section of the International Congress of Applied Chemistry held in London in 1909, and was a member of the advisory committees and juries of several of the exhibitions held in London and elsewhere.

G. T. H.

FRANCIS HENRY NEVILLE.

BORN DECEMBER 2ND, 1847; DIED JUNE 5TH, 1915.

BY the death at his home at Letchworth on June 5th, 1915, at the age of sixty-eight, the Society has lost in F. H. Neville a man of most versatile gifts. Trained as a mathematician, he retained throughout his life the habit of close reasoning and the power of applying his mathematics to the problem he had before him.

In conjunction with C. T. Heycock he published a number of papers on alloys in the Chemical Society's *Transactions* and in the *Proceedings* and *Transactions of the Royal Society*. The earliest of these papers appeared in the *Proceedings* of the Chemical Society for March 21st, 1889, and they were continued at intervals to 1914. Neville also contributed the article on alloys to the "Encyclopædia Britannica." It is difficult to realise how much work has been carried on on the subject of alloys since the first paper was published and to appreciate the difficulties that had to be overcome. At the time the work was commenced we had to depend almost entirely on mercury thermometers, and it was impossible to determine temperatures above the melting point of lead with any approach to accuracy.

Fortunately Messrs. E. H. Griffiths and H. L. Callendar published their work on platinum resistance thermometry about this

time, with the result that the measurement of high temperatures became comparatively easy. Neville threw himself into this work with characteristic energy and thoroughness. The table of freezing points of metals, published in the Chemical Society's *Transactions*, 1894–1895, up to and including the freezing point of copper, contains the results of the early work with the platinum thermometer, and has with a few exceptions never been seriously altered.

The heaviest piece of work undertaken was on the constitution of the copper–tin alloys; this formed the subject of the Bakerian Lecture in 1903. The many beautiful photographs which accompany the text of this lecture as published in Vol. **202** of the *Philosophical Transactions* were largely Neville's work.

The few who had the privilege of knowing him intimately were aware that he was a man of exceptional ability and wide reading, for he was deeply interested in art, history, and literature, and he spoke fluently French, German, and Italian.

The high esteem he was held in by his friends and former pupils in Cambridge was recently marked by the presentation of his portrait, by Mr. Charles Shannon, to his College. He was elected a Fellow of Sidney Sussex College in 1871, and a Fellow of the Royal Society in 1897. As the intimate friend and co-worker of Neville, it is impossible for me to do justice to the memory of one of the most charming personalities it has ever been my good fortune to meet.

C. T. Heycock.

THOMAS LAW PATTERSON.

Born January 17th, 1842; Died May 7th, 1915.

Thomas Law Patterson, the eldest child of George Patterson, merchant, Grey Abbey, Belfast, was born in Glasgow. His early years were passed at Grey Abbey, but he received his later education at Glasgow Academy, and in 1860 entered the employment of Mr. Hugh Donaghy, a chemical manufacturer in Glasgow. His interest in chemistry being aroused by the nature of his occupation, he attended Dr. Penny's Friday evening lectures during the Sessions 1862–1863 and 1863–1864, and the Thursday evening practical class during the former, together with Dr. Wallace's Tuesday evening lectures during the latter, period. In November, 1863, he became junior assistant, and, subsequently, senior assistant to Dr. Machattie, and in 1865 was appointed chemist in Mr. John Poynter's works at Greenock. In 1868 he became chief chemist to Messrs. John Walker and Co., sugar refiners, Greenock.

This post he resigned in 1872, in order to start an analytical business in Greenock in partnership with the late Mr. T. R. Ogilvie, the firm acting as public analysts for the burgh. In 1874 Mr. Patterson was asked to assume the managership of Messrs. John Walker and Co.'s refinery, in which capacity he acted for twenty-three years, devoting himself unsparingly and with much success to his duties. He was a man of great energy and indomitable perseverance, and owing largely to these qualities as well as to his scientific outlook and engineering ability, the works were much enlarged and improved and became amongst the most modern in the country.

He retired in 1897, but continued to practise until his death as a consulting chemical technologist and sugar specialist.

He took out several patents for improvements in the refining of sugar, the best known of these being perhaps a special centrifugal for steaming sugar; another, which he took out later, for a syrup classifying apparatus for attachment to centrifugals, was also successful.

He was always much interested in the purely scientific aspect of all the problems with which he had to deal, as appears from his published papers. As far back as 1873, in connexion with his analytical practice, he had devised a method for estimating, in solution, substances exhibiting absorption spectra. Later he improved this method, and published an account of his apparatus (*J. Soc. Chem. Ind.*, 1890, **9**, 36). His method consisted in passing white light through two tubes placed side by side, one containing a standard solution of the substance to be estimated and the other the unknown solution. These beams of light were then thrown by reflection on to a slit, passing afterwards through a direct vision prism in such a way that two spectra were seen one above the other. The absorption bands from the respective solutions could then be compared and adjusted to equal intensity by alteration of the depth of either column of liquid. The method was shown to be capable of estimating so small a quantity as 0·00294 per cent. of eosin in a sweetmeat, and to be suitable for the estimation of alizarin in cloth, or erythrosin in paraffin candles, and in other ways.

Another subject which had naturally forced itself on his attention was animal charcoal. He had published notes regarding it from time to time, and, after his retirement from active work in the refinery, he fitted up a small laboratory at his own residence in order to continue an investigation which he had carried on at intervals for many years previously. Although, in the manufacture of char, the bones are submitted to a red heat for at least twelve

hours, there nevertheless remains in it an organic substance still containing nitrogen. Part of this may be extracted by cold concentrated sulphuric acid, and further portions may be extracted by boiling with sulphuric acid several times. The substance extracted is thrown out of the acid solution by ten to twelve volumes of water as a gelatinous, brown precipitate. This compound, in the moist condition after precipitation, was found to decolorise caramel solution, the portion obtained by extraction with cold sulphuric acid having about sixteen times the power of good animal charcoal, whilst that which had been extracted with boiling sulphuric acid was more than forty times as effective. In the dry state this compound has a horny appearance and a conchoidal fracture; it differs in composition less than might have been expected from ox-bone cartilage. In this condition its decolorising power is slightly inferior to that of an equal weight of charcoal (*J. Soc. Chem. Ind.*, 1903, **22**, 608).

Another paper which may be mentioned, the last he published, was a "Study of a Falling Factory Chimney" (*Proc. Roy. Phil. Soc. Glas.*, 1912, **43**, 217), in which, from a number of unco-ordinated photographs taken of the demolition of an old chimney-stack in Greenock, he traced with success the manner in which the fall occurred.

Mr. Patterson was much interested in Egyptology; he was for many years a keen photographer, and he was also a very capable microscopist. He was closely identified with various philanthropic and religious activities, and was for a time a director of the London Missionary Society. He was a Fellow of the Chemical Society from March 17th, 1870, until his death; he was an original Fellow of the Institute of Chemistry, and an original member of the Society of Chemical Industry.

Although he had been failing somewhat during the last few years, and was subject to attacks of bronchitis, he died rather suddenly, from heart failure, on May 7th, 1915, after a short illness. He had married, in September, 1871, Margaret Richmond Stewart, third daughter of David Stewart, merchant, Glasgow, by whom, with two sons, he is survived.

T. S. P.

JAMES HOLMS POLLOK.

BORN AUGUST 9TH, 1868; DIED NOVEMBER 26TH, 1915.

JAMES HOLMS POLLOK, second son of the late Morris Pollok, was born at Mansion House, Govan, Scotland, and received his early education at the High School in Glasgow.

As a schoolboy, his chief pleasure consisted in experimenting with chemicals, first at home and then in an outhouse to which he was relegated by his father for obvious reasons. He eventually succeeded in blowing up the latter edifice, after which escapade he was sent to study chemistry in the University of Glasgow in 1883. His chemical teacher was Professor Ferguson, and he also attended Lord Kelvin's classes in natural philosophy. In afterlife he always recalled with gratitude the kindness and inspiration received from these eminent masters. He graduated as B.Sc. in 1887, and was then appointed junior assistant to the Professor of Chemistry in the University.

While holding this post Pollok worked out an improved process for the extraction of gold by chlorination. This improvement, which was patented (English Patent 17495 of 1887), was based on " the production of pressure in the vessel wherein the wet process or method of extracting gold by chlorination is conducted by forcing water into the said vessel by means of a hydraulic pump, accumulator, or other water-forcing apparatus."

After a successful lawsuit, whereby the validity of the patent was established, several companies were started to exploit this process, which gave better results than chlorination under atmospheric pressure, and Pollok resigned his post in the University in order to devote himself to the development of these industrial undertakings. Additional patents were filed (English Patents 16796 of 1888 and 5578 of 1889), and the process was put into operation in various goldfields. He went first to Johannesburg and subsequently to Queensland to superintend the erection and starting of chlorination plants. This invention, like other chlorination methods, did not, however, meet with enduring success, being soon afterwards superseded by the cyanide process.

Pollok then returned to academic work, and in 1896 was appointed assistant chemist in the Royal College of Science for Ireland. In ths capacity he also acted as instructor in assay. He retained this post until 1913. By this time the Royal College of Science had been moved from its old home in Stephen's Green to the new and far larger buildings in Upper Merrion Street. This change led to considerable extension in equipment and laboratory facilities, and, as regards the chemical division, to a further development in the direction of applied chemistry. The need for advanced teaching in physical chemistry and metallurgy had become imperative, and the Department of Agriculture and Technical Instruction for Ireland, recognising that Pollok possessed in an exceptional degree the personal and scientific qualifications for effectively carrying out this work, promoted him to be Lecturer in Physical

and Metallurgical Chemistry. In this new office he arranged lecture and laboratory courses for students of the Faculty of Applied Chemistry and also for students of the Engineering Faculty.

In 1915 the Department decided to carry on the preliminary scientific work of the Royal Veterinary College of Ireland in the Royal College of Science, and it fell to Pollok's lot to undertake the additional task of teaching physics and chemistry to this new class of students. He was actively engaged in this work when death overtook him last November.

The list of Pollok's published contributions to chemistry and spectroscopy (*Chem. Soc. Decennial Indexes*, 1893–1902, p. 521; 1903–1912, p. 912), which comprises twelve papers published chiefly in the *Scientific Proceedings* of the Royal Dublin Society, does not do justice to his great activity and keen, unflagging interest in original research, but his investigations usually had an industrial bearing and did not lend themselves to publication.

Even as a student, however, he showed considerable power of accurate observation, and his earliest publication was a paper communicated on his behalf by Lord Kelvin (then Sir William Thomson) to the Royal Society of Edinburgh in 1886. This contribution was entitled, "Comparison of the Volumes of Saline Solutions with the Sums of the Volumes of the Constituents," and the subject was suggested to Pollok by an experiment he had seen in Thomson's lectures. Measurements were made of the contractions produced by dissolving in water various soluble chlorides, sulphates, and carbonates. The curves representing variations in contractions produced by changes in dilution were found in the case of these salts to be of the form of equilateral hyperbolas. Non-saline substances, such as alcohol, gave very different results.

For more than ten years Pollok's energies were absorbed in the exploitation of his patented processes for gold-extraction, and it was not until 1899 that he appeared again as a contributor to scientific literature. A note on the thermal effects of dilution was followed by an analytical study of diatomaceous earth (kieselguhr) from County Antrim. The deposits of this material, which are found along both banks of the Lower Bann below its emergence from Lough Neagh, rest on peat, and are covered merely by vegetation; they consist chiefly of diatoms of pill-box shape, which are less suitable for dynamite manufacture than the fusiform varieties. In spite of this disadvantage, however, a considerable trade has been established in these deposits, the material being sold as polishing powder, as a soap-filler, and as an insulating substance in the manufacture of non-conducting bricks.

During the next few years Pollok devoted himself to the study of glucinum and its compounds. For this purpose he worked with the beryl of Limoges and also with the local variety of this mineral obtained from the Glencullen quarries in County Wicklow. He determined the heats of formation and solution of anhydrous glucinum chloride, and compared these data with the corresponding constants for the chlorides of magnesium and zinc. This comparison showed that the rise in atomic weight of the metals of this periodic family is accompanied by a diminution in the heats of formation and solution of their anhydrous chlorides.

For a thesis on these researches on glucinum Pollok was in 1905 awarded the degree of D.Sc. in the University of Glasgow.

Further work on the beryl led him to the conclusion that the several fractions obtained on distilling anhydrous glucinum chloride showed a variation in the chemical equivalent of the contained metal. There was a touch of sentiment in the names, hibernium and scotium, which he suggested tentatively for the two hypothetical constituents of glucinum. Although subsequent investigators have not confirmed this view of the composite nature of glucinum, yet Pollok's laborious study of the beryl rendered available for other researches purified specimens of glucinum salts which are plentiful materials in the college laboratories even at the present time.

The next phase in Pollok's scientific career shows plainly the influence of Sir Walter (then Professor) Hartley, who by this time had established in the Royal College of Science an important centre of spectroscopic research. During five years Pollok contributed eight memoirs on spectroscopy to the Royal Dublin Society, partly alone and partly in collaboration with Dr. A. G. G. Leonard. The object of these investigations was to render more quantitative the spectroscopic indications presented by different metals when their solutions were sparked between gold electrodes, or when the free metals were vaporised in quartz vacuum tubes. The data thus obtained were utilised in spectrographic analyses of metals and alloys. For instance, the impurities in a specimen of commercial gallium were found to be lead, tin, copper, and aluminium.

Pollok's devotion to this department of scientific research had a deplorable effect on his health. In 1913 he developed an exceedingly intractable form of eczema induced by the rays from his vacuum tubes. The relation between cause and effect was plainly demonstrated in this affliction, for the eruption occurred on the hand and on that side of the face which had been exposed to the radiations during the manipulation of the spectrograph.

Acting under medical advice, Pollok obtained six months' leave,

which was spent in Southern Europe and in Cyprus. Returning to Ireland in the spring of 1914, he appeared to have recovered completely from the epidermal trouble. He had during his stay in Cyprus made a survey of certain copper deposits on the island, and he brought home many specimens of minerals and also samples of salt and salt water from the lagoon at Larnaca. He now devoted all his spare time to the analysis of these materials, and on the results of his assays of the copper minerals he formed a small private syndicate in order to open up the copper deposit he had prospected. He also endeavoured to arouse public interest in the Larnaca lagoon, the extremely salt water of which he found to contain a very appreciable amount of combined bromine.

In August, 1914, he re-visited Cyprus and satisfied himself that the copper property was not a payable proposition. On his return to Ireland he continued to work at the Larnaca salts and other Cyprian products. He also turned his attention to the extraction of potash from Irish felspar and mica. These technical investigations did not, however, monopolise his activities, and as a war service he qualified in first aid and assisted in organising the Royal College of Science Voluntary Aid Detachment, of which unit he was the very efficient quartermaster. On every occasion on which wounded soldiers were landed in Dublin he performed meritorious services in conducting them to their allotted hospitals and in entertaining them during convalescence. He was assiduous in the duties of training this detachment, and on the Saturday preceding his death he was on parade in uniform, although suffering acutely from the illness to which he shortly succumbed. At the end of the drill he bade me farewell in the best of spirits, referring lightheartedly to an abdominal operation he was to undergo on the following Tuesday. On Wednesday I inquired at the nursing home, and the prognosis was not unfavourable. The following day, however, there was a change for the worse, and on Friday he passed away. The news of his unexpected end came as a stupefying shock to his colleagues and students, who had confidently anticipated his return in a few weeks.

Pollok was a very successful teacher, and invariably gained the enthusiasm and affection of his students, especially those who worked through his courses in metallurgy and assay. A skilful and neat manipulator, he was a jealous custodian of the fine equipment which a generous Treasury grant has placed at the disposal of the Faculty of Applied Chemistry. Herein lies the essential tragedy of Pollok's premature death. He had always hoped to commence a fresh lease of his scientific career in the utilisation for physico-chemical research of the splendid instruments which he had person-

ally selected and safeguarded. Among his unfinished work is a text-book on spectroscopic analysis, which is being completed by his former pupil, Dr. Leonard.

In his youth a seeker after gold, Pollok had journeyed far in many lands. Although possessed of very decided views on controversial topics, his travels had taught him the virtue of tolerance. He was always prepared on second thoughts to qualify a hastily expressed opinion, whilst his natural charm of manner disarmed the criticism even of those who differed fundamentally from him.

Pollok had made many excursions to Asia Minor and the Levant, and he was well acquainted with the characteristics of the races inhabiting those regions. He was a warm admirer of the Turkish character, and Turkey's adherence to the cause of the Central Powers, under the baleful influence of the Young Turk Party, was a profound disappointment to him. He had imbibed not a little of the Moslem fatalism and philosophy. A favourite quotation of his to relatives and intimates was the Turkish saying that "Death is the gate of Paradise." It was with the cheerful stoicism inspired by this belief in the imminence of "the land o' the leal" that he serenely faced his fatal malady.

> "So when the Angel of the darker Drink
> At last shall find you by the river-brink,
> And, offering his Cup, invite your Soul
> Forth to your lips to quaff—you shall not shrink."

Pollok was widely respected in scientific circles. He was a member of the Royal Irish Academy, and had officiated as Chairman of the Science Committee of the Royal Dublin Society. For many years he was secretary, and afterwards treasurer, of the Dublin Scientific Club. He had achieved a well-earned reputation as an industrial chemist, and was ever alert to new openings in applied chemistry which might benefit his adopted country. By his death Ireland has lost a very earnest and able scientific worker. Nowhere is this bereavement felt more deeply than in the Department of Agriculture and Technical Instruction for Ireland, where he was held in great esteem and affection by all his colleagues.

He leaves behind a widow and two daughters to mourn his loss.

GILBERT T. MORGAN.

THE RIGHT HONOURABLE SIR HENRY ENFIELD ROSCOE.

BORN JANUARY 7TH, 1833; DIED DECEMBER 18TH, 1915.

HENRY ENFIELD ROSCOE was born in London on January 7th, 1833. His father, Henry Roscoe, was a barrister, who became judge of the Court of Passage, Liverpool. His grandfather was William Roscoe, a banker in Liverpool, and in 1806 Liberal Member of Parliament for that borough. He was a man of remarkable attainments, a generous patron of the Arts, and known in the history of literature as the author of the "Lives" of Lorenzo de Medici and Leo X. Roscoe's mother's maiden name was Maria Fletcher, the daughter of a respected Liverpool merchant, who was chairman of the West Indian Committee. Her maternal grandfather, Dr. William Enfield, author of the well-known "Speaker," a man distinguished for soundness of literary judgment, was the last Rector of the Warrington Academy, in which Joseph Priestley, the chemist, was a tutor.

Roscoe's father died when he was about four years old. After a few years at a preparatory school, he was sent to the High School of the Liverpool Institute, one of the earliest of the so-called modern schools. Here he came under the influence of Hugo Reid, a well-known teacher and writer on natural philosophy, and of W. B. Hodgson, an excellent teacher of English, who afterwards became Professor of Political Economy in the University of Edinburgh. The school possessed a chemical laboratory under the direction of W. H. Balmain, the discoverer of "luminous paint" and of boron nitride, and one of the early contributors to the then newly-founded Chemical Society. He was a stimulating and original teacher, and to him is due the credit of introducing Roscoe to the study of chemistry.

In 1848 Roscoe was entered at University College, London, at that time the only seat of higher learning and research in England open to men who were refused admittance to the older Universities on denominational grounds. Of his teachers at Gower Street, the one who most influenced his career was Thomas Graham. In entering Graham's class-room, Roscoe found himself in a new world, and one indication of the eagerness with which he exploited it may be gleaned from the fact that at the end of his first session he had gained the silver medal in chemistry.

Roscoe now elected to follow chemistry as a career. He entered the Birkbeck Laboratory, then under the charge of Williamson, whom Graham had recently brought over from Paris, where he had

been working with Laurent and Gerhardt. In his second year Roscoe became Williamson's private assistant, and took part in his researches, and when Graham accepted the Mastership of the Mint, and Williamson succeeded to his chair, Roscoe was made lecture assistant.

It was in recognition of Roscoe's association with Williamson that he was deputed, nearly forty years afterwards, to present, on behalf of the subscribers, the portrait of his master which now hangs in University College.

Having taken his B.A. degree, with honours in chemistry, he decided to enlarge his experience by a course of study in a Continental laboratory, as was then the usual custom. He elected to go to Bunsen, who had recently been called from Breslau to Heidelberg in succession to Leopold Gmelin, the author of the well-known "Handbuch." Bunsen had already won for himself a European reputation by his masterly investigation of the cacodyl compounds, by his methods of gas-analysis, his studies of the chemistry of the blast-furnace, his invention of the carbon–zinc battery and photometer, and his inquiries into the chemical aspects of the volcanic and pseudo-volcanic phenomena of Iceland.

In the cloisters of the old monastery which then did duty as the Heidelberg laboratory, Roscoe was first indoctrinated into the art and mystery of quantitative chemical analysis, and he there acquired that familiarity with Bunsen's methods and with his system of laboratory instruction that he was to turn to such signal account in the establishment and direction of the Manchester School of Chemistry.

One of his earliest quantitative exercises was in silicate analysis, and his first published paper was a joint production with Schönfeld on the composition of certain varieties of gneiss. This appeared in *Liebig's Annalen* for 1854.

At the close of his second session he passed his doctor's examination *summa cum laude*, and then embarked on the well-known inquiry, in association with Bunsen, on the measurement of the chemical action of light, which occupied much of his time and energy during the next eight years.

In the obituary notices he wrote for *Nature* of August 31st, 1899, and for the *Proceedings of the Royal Society*, and more especially in the admirable Memorial Lecture he gave to the Chemical Society, Roscoe did ample justice to the memory of Bunsen as a great chemist, pre-eminent as a discoverer and teacher, and lovable as a true and noble-hearted man.

The Memorial Lecture was reprinted in America by the Smithsonian Institute, and was translated into German to be prefixed to

the collection of Bunsen's works published by the Bunsen-Gesellschaft, a society founded in his honour. In the course of their long friendship Roscoe received many letters from his illustrious master. These—126 in number—were suitably bound and presented by him to the Bunsen Society.

In the autumn of 1856 Roscoe returned to London, and, with the help of friends, set up a private laboratory, with Wilhelm Dittmar to assist him in research work. He also obtained employment as a science lecturer at an army school at Eltham, and did some analytical work on ventilation for a Departmental Committee, the results of which were published by the Chemical Society. The London laboratory was, however, soon given up, for in the following year the late Sir Edward Frankland, the first professor of chemistry in the recently founded Owens College, Manchester, having resigned his appointment, Roscoe offered himself as a candidate for the chair and was elected. The college had been established for about six years in a private house in the vicinity of Deansgate which had formerly been the residence of Richard Cobden. It had at the time some half-dozen professors and about thirty-five students, fifteen of whom were working in the chemical laboratory which had been fitted up by Frankland.

The college at this period of its existence was at the lowest ebb of its fortunes. It was written down by the local Press as "a mortifying failure," and its financial condition was such that the new professor was refused the tenancy of a house when the landlord learned that he was one of its staff. In the Manchester of those days there was little appreciation of the bearing of science on an industrial career. The college was the first attempt of the kind to bring the higher training and something of the spirit of collegiate life within the reach of the middle-class youth of a great business community, and it was necessary to have some regard to the special requirements of the district as well as, it may be, to its prejudices.

Roscoe's antecedents, his associations with Lancashire, and his knowledge of and sympathy with what is best in the Lancashire character made him quick to realise the conditions upon which the success of the struggling institution must depend. He saw that it was of no use for it to set itself athwart the economic life of the community, and, young as he was—he was twenty-four—he was more alive to the practical necessities of the position than the majority of his colleagues or indeed of the governing body. It was his immediate aim to establish at Owens College a school of chemistry which should worthily serve the interests of the great manufacturing district of South Lancashire. From the outset he

threw himself heartily into the educational and scientific activities of the town in which was to be his home for the next thirty years. He joined the Philosophical Society of Manchester, so honourably associated with the names of Dalton, Joule, and Schunck; for many years he served as its secretary, was a frequent contributor to its publications, and ultimately became its president and an honorary member. He was the first recipient of its Dalton medal, awarded in recognition of his elucidation of the genesis of Dalton's great theory, based on manuscripts and laboratory note-books in the possession of the Society, and published in association with his pupil and friend, Dr. Harden.*

The visit of the British Association to Manchester in 1861, when he served as one of the local secretaries, afforded him an opportunity of showing his organising power and business aptitudes. These were still further demonstrated in the winter of 1862, during the memorable cotton famine in Lancashire, when he acted as one of the secretaries to a committee created to provide some form of intellectual occupation for the thousands of operatives thrown out of employment by the stoppage of the staple industry of the district. He gave experimental lectures on subjects likely to attract a working-class audience. These were highly popular, and undoubtedly awakened a general interest in scientific matters. Their success encouraged him to institute the series of Science Lectures for the People which he began in 1866 and carried on for eleven consecutive winters. In this movement he secured the co-operation of Huxley, Carpenter, Tyndall, Huggins, Lord Avebury, Abel, Stanley Jevons, Clifford, Spottiswoode, and others. The lectures were given in some of the largest public halls in the city, and were attended by thousands. They were published week by week as delivered, and were sold for a penny all over the world.

Of their stimulating influence Roscoe received abundant testimony; in after life he frequently met persons, some occupying high and responsible positions in commerce and industry, who informed him that they were indebted to these lectures for their first interest in science.

Services such as these, combined with Roscoe's growing popularity and influence in the district, necessarily reacted favourably upon the fortunes of the college, and especially of its chemical department, and the laboratory soon became inadequate to accommodate the students who came to it from all parts of England. The prospects of the college were now so well assured

* *A New View of the Origin of Dalton's Atomic Theory.* By H. E. Roscoe and A. Harden. Macmillan and Co.

that, in 1867, a town's meeting resolved "that the time had come for the public of the district to unite for the purpose of developing the college on a more comprehensive scale, and in appropriate and convenient buildings." An executive committee, on which Roscoe was placed, was appointed to carry out this resolution, and he was called on to serve on certain sub-committees dealing with the new site, buildings, and extension and rearrangement of courses of study. It says much for the influence and power he had now acquired in the councils of the college, and for the confidence reposed in his judgment and business capacity, that he should be called upon to take so prominent and so responsible a share in the extension movement. The foundation-stone of the first block of buildings to be erected was laid by the Duke of Devonshire, the first president of Owens College, on September 23rd, 1870.

The design of the new chemical laboratories was wholly inspired by Roscoe after examining every Continental example that might furnish suggestions concerning internal arrangements and fittings, the details being admirably carried out by the late Mr. Alfred Waterhouse. It is not too much to say of these laboratories that they have served as models for practically every chemical laboratory connected with a collegiate institution that has been subsequently built in this country or abroad.

As the college grew and prospered, and as the scheme of its studies was gradually enlarged until it included nearly every department of learning professed at the older Universities, it was inevitable that sooner or later it should seek for University powers. Many distinguished friends of the college, among them Lord Kelvin and Sir Benjamin Brodie, who had long been interested in its development, were of opinion in the late 'seventies that it had already attained a university position, and that steps should be taken to make it the University of Manchester. The idea of a university for Manchester was as old as 1640, when it was mooted by Henry Fairfax, Rector of Ashton-under-Lyne, and it cropped up again in the latter half of the eighteenth, and also in the early part of the nineteenth century, and it was but natural that it should gradually centre itself around the foundation of John Owens. To Roscoe and his colleagues, Sir A. W. Ward, who was then Professor of History at the college, Principal Greenwood, and Professor Morgan, belong the credit of taking the first effective steps towards the realisation of this consummation. "It is to the zeal and untiring devotion of these four gentlemen," wrote Mr. Thompson, the historian of Owens College, "that Manchester owes its university; others cordially supported the movement, but

they through five weary years placed their case before the public, removed prejudices, advanced good arguments, and lived down opposition."

Opposition, it should be stated, mainly came from Yorkshire, as it had threatened to come in Fairfax's time. The newly-founded Yorkshire College in Leeds considered that its future was jeopardised by the establishment of a university so close to the borders of its own area, and whilst not opposed to the creation of another university in the north of England, prayed that its charter might be so modified as to admit of the inclusion of other institutions of collegiate rank which might be able to fulfil the conditions of incorporation as constituent colleges with a definite share in its government.

This action resulted in the establishment in 1880 of a federal university—the Victoria University—in which Owens College, University College, Liverpool, and the Yorkshire College, Leeds, were the constituent colleges, with its seat in Manchester. The elevation of Mason's College to the dignity of the University of Birmingham was quickly followed by the dissolution of the federal university in Manchester, and each constituent college in time received its own charter as an independent university.

Some years before Owens College attained to the position of a university, attempts were made to induce Roscoe to sever his connexion with it. In 1870 he was offered the lectureship on chemistry at St. Bartholomew's Hospital in succession to Dr. Matthiesson, and two years later he was invited to become a candidate for the vacant chair of chemistry at Oxford, with the promise of a fellowship if elected. That he might be Brodie's successor was, he says, a tempting suggestion, but on consideration he felt he had a wider scope and the possibility of greater usefulness in building up the chemical school of Owens College—a decision which he had the satisfaction of knowing met with the warm approval of Huxley and other friends.

Roscoe's method of working his department was wholly modelled on that of Bunsen, as those of his pupils who subsequently repaired to Heidelberg could testify. He gave his lectures at the beginning of the working day, when he retired to his sitting-room to glance through his correspondence whilst the laboratory men were settling to work. He would then go round to each in turn, see what had been done since the previous visit, and give such directions as were necessary. Although the students worked independently and were at different stages of progress, he always knew how each was occupied. With the men engaged on research work or with preparations or on any matter out of the usual routine he would

frequently spend a considerable amount of time. He always seemed to be as much interested in the work as the workers themselves, and was unaffectedly pleased with a good analytical result, a well-constructed apparatus, or a neat preparation. His boyish love of manipulation, simply as such, remained with him to the end, and he somehow managed to convey something of his own feeling of delight in handling apparatus to those he taught. In this lay the secret of his power and success as the director of a laboratory. Although his students never forgot that he was the professor—he was always "Doctor Roscoe" to them—they realised that he was on an easily approachable plane, and a bond of sympathy and mutual understanding was quickly established which strengthened into friendship and esteem. Of course, as the number of his pupils increased, and the laboratories became larger and more numerous, it became impossible to give so large a share of individual attention, and much had to be delegated to demonstrators, for the most part chosen from among senior students who were preparing for an academic career. But he was quite alive to the value of "new blood," and any promising young man who had shown aptitude for teaching or ability in research work that he could hear of was always sympathetically considered when an appointment had to be made.

He next visited his private laboratory to consult with his assistants and to learn of the progress of their work. As his engagements multiplied, and the calls upon his time increased, he gradually ceased to take any active part in the operations when assured of the competency of those to whom he had entrusted the execution of his plan of research. Indeed, he allowed his chosen helpers considerable latitude if, as usually happened, they were genuinely interested in their work. He had a strong belief in the wisdom of giving the 'prentice hand "his head" as the surest way of strengthening any latent faculty for original inquiry he might possess. He had himself been trained in this way, and he employed the same method in turn.

Roscoe, like Bunsen, set no very great value on lecture-room teaching, although he recognised that with the majority of students no other system is practicable. A lecture course no doubt serves to afford an *aperçu* of the subject, which is what the average attendant at lectures presumably wants. At the same time he spared no pains to make his lectures interesting, and they were always admirably illustrated by experiments. Luckily, he had in his *famulus* Heywood, a remarkably able lecture-assistant, a skilful glass-blower, and a good mechanician, with a talent for devising striking and original illustrations. Roscoe had a good voice, clear

enunciation, and a pleasant, easy mode of delivery, but he had none of the arts of the orator. In the lecture-room his language was simple and direct; he was an excellent expositor, lucid and instructive, and never dull.

Although organic chemistry, at his most active period as an investigator, was experiencing an extraordinary development and offering limitless opportunities of discovery, its problems then and, it may be added, at no subsequent time, had more than an academic interest for him. The only communication dealing with organic chemistry with which his name is associated is a short note on the spontaneous polymerisation of volatile hydrocarbons, contributed to the Chemical Society in 1885.* The paper had its origin in an observation brought to his notice by a tar distiller, who had observed the formation on standing of a white, crystalline mass, resembling camphor, resulting from the decomposition of phenolic substances at a red heat. The crystalline substance was found to have the molecular formula $C_{10}H_{12}$, but its real nature and the mode of its genesis were not made out.

Organic chemistry was scarcely taught at Heidelberg in Roscoe's time, and then only by subordinate professors and *privat-docenten*, mainly to pharmacists. Kekulé had attempted to establish himself as a *privat-docent* in organic chemistry in Heidelberg, but his first success as a teacher came to him in Ghent. But Roscoe at this time was probably too much occupied with his work under Bunsen to give much attention to any other field of chemical inquiry. The effect of this training was seen in the subsequent character of his teaching. The lectures on organic chemistry that he was necessarily required to give at Owens College, with their limited possibilities of experimental illustration, simply bored him, and, it may be added, had no very stimulating effect on his hearers. Happily, he found in Schorlemmer a colleague who was well fitted in many respects to relieve him of the duty. Schorlemmer was not a fluent speaker, and although he wrote our language with ease and accuracy, he never acquired familiarity with the peculiarities of its pronunciation. But he was a remarkably well-read man with an astonishingly retentive memory, fully abreast of the organic chemistry of his time and keenly interested in every phase of its development. He was, moreover, an excellent teacher, and his lectures were thoroughly appreciated by the discerning student.

The character of Roscoe's work in original inquiry may also be

* "Note on the Spontaneous Polymerisation of Volatile Hydrocarbons at the Ordinary Atmospheric Temperature." By H. E. Roscoe (T., 1885, **47**, 669).

said to have been entirely moulded by his Heidelberg training, and Bunsen's influence may be traced throughout it. So completely was this the case that, consciously or unconsciously, he seemed never to contemplate attacking any problem that would not have appealed to or have been appreciated by Bunsen. His first research was undoubtedly suggested by Bunsen. As already stated, it resulted in the classical investigation on the laws regulating photochemical action. It was already known that a mixture of equal volumes of chlorine and hydrogen on exposure to light lost its characteristic colour and was converted into hydrogen chloride readily soluble in water. Bunsen conceived the idea of making this reaction the basis of a method of measuring the relative amount of activity of the light-vibrations which are concerned in effecting chemical change. As a matter of fact, the idea was not new, for, unknown to Bunsen, it had already been adopted by Draper, of New York, who had, as he states in his paper in the *Philosophical Magazine* for December, 1843, "invented an instrument [based upon the same reaction] for measuring the chemical force of the tithonic rays which are found at a maximum in the indigo space, and which from that point gradually fade away to each end of the spectrum."

It perhaps says little for the assiduity with which the young investigator read the original chemical literature of his time that he should only have acquired knowledge of Draper's remarkable papers some thirteen years after they were published in the English journals; but the chemical students of University College in those days had far fewer opportunities of access to original literature than they now enjoy.

Roscoe's disconsolance on learning that he had been thus anticipated was probably of no long duration. "Do not," wrote Bunsen in reply to the distressing information, "let your discovery of Draper's work disconcert you. . . . It appears to me that the value of an investigation is not to be measured by whether something is described in it for the first time, but rather by what means and methods a fact is proved beyond doubt or cavil, and in this respect I think that Draper has left plenty for us to do."

After many fruitless attempts they succeeded in constructing an apparatus in which the defects of Draper's "tithonometer" were obviated, and by which not only accurate comparative determinations could be made, but which enabled them to reduce the chemical action of light to absolute measure. They showed by means of it that the amount of chemical action produced by light from a constant source varied inversely as the square of the

distance. They studied more accurately the phenomena of photochemical induction discovered by Draper and the causes which determine its occurrence, and the laws which regulate the chemical action of light after the induction is completed. They proved that the absorption of the chemical rays in passing through a medium varies directly as the intensity of the light, and that the amount transmitted varies proportionally with the density of the absorbing medium. It was found that for a given amount of chemical action effected in the mixture of chlorine and hydrogen an equivalent quantity of light is absorbed, and that the coefficients of extinction of pure chlorine for chemical rays from various sources of light are very different. They established a general and absolute standard of comparison for the chemical action of light, and sought to determine the quantitative relations of the chemical action effected by direct and diffused sunlight, and to investigate the laws which regulate the distribution on the earth's surface of the chemical activity emanating from the sun. They also measured the chemical action of the constituent parts of the solar spectrum. The action on the sensitive gaseous mixture showed the existence of several maxima of chemical intensity in the spectrum. The greatest action was observed between the lines *G* in the indigo and *H* in the violet, whilst another maximum was found to be near the line *I* in the ultraviolet. Towards the least refrangible end of the spectrum the action became imperceptible above the line *D* in the orange, but at the other end of the spectrum the action was found to extend as far as Stokes's line *U*, or to a distance from the line *H* greater than the total length of the ordinary visible spectrum.

By investigating the conditions under which it was possible to prepare a photographic paper of uniform and constant sensitiveness, and ascertaining the means by which the darkening of the paper on insolation could be accurately compared with a standard tint, it was found comparatively easy to construct an instrument capable of measuring the chemical action of light effected at any point on the earth's surface by the total sunlight and diffuse daylight in the most widely varying circumstances of climate and atmospheric condition.

This joint research, begun in 1855, occupied its authors until 1862. Roscoe did most of the experimental work, and after his election to the professorship in Owens College in 1857 he spent the greater part of each long vacation in Heidelberg in continuing the inquiry.

The results were communicated to the Royal Society in a series of memoirs, which are published in the *Philosophical Trans-*

*actions.** Subsequently he pursued the subject alone or in association with others. In a short paper, published in 1863, he made a series of measurements of the chemical brightness of various portions of the solar disk by means of standard photographic paper, according to the method described by Bunsen and himself in their last communication,† and in 1864 he described a method of meteorological registration of the chemical action of total daylight, based on a modification of that originally used by Bunsen and himself. The account of this method was made the Bakerian Lecture of 1865, and is published in the *Philosophical Transactions* of that year.‡

In this paper he gives the results of consecutive observations on each day for nearly a month at about midsummer, and compares the chemical action of light at Manchester at the winter and summer solstices and the vernal and autumnal equinoxes. The wide variation in the chemical action of light at different periods of the year was illustrated by the fact that if the integral of that on the shortest day be taken as unity, that upon the equinox will be represented by 7 and that upon the longest day by 25.

In 1866 Mr. Baxendell and he contributed a joint note to the Royal Society on the relative chemical intensities of direct sunlight and diffuse daylight at different altitudes of the sun. They showed from observations made at Manchester and at Heidelberg that the ratio of the chemical intensity of direct to diffuse sunlight for a given altitude at different localities is not constant, but varies with the transparency of the atmosphere, and that this ratio does not in the least correspond with the value of visible

* "Photochemical Researches." By R. W. Bunsen and H. E. Roscoe :
Part I.—"Measurement of the Chemical Action of Light" (*Phil. Trans.*, 1857, **147**, 355).
Part II.—"Phenomena of Photo-chemical Induction" (*Phil. Trans.* 1857, **147**, 381).
Part III.—"Optical and Chemical Extinction of the Chemical Rays" (*Phil. Trans.*, 1857, **147**, 601).
Part IV.—"Comparative and Absolute Measurement of the Chemical Rays; Chemical Action of Diffuse Daylight; Chemical Action of Direct Sunlight; Photo-chemical Action of the Sun compared with that of a Terrestrial Source of Light; Chemical Action of the Constituent Parts of Solar Light" (*Phil. Trans.*, 1859, **149**, 879).
Part V.—"On the Direct Measurement of the Chemical Action of Sunlight" (*Phil. Trans.*, 1863, **153**, 139).

† "On the Measurement of the Chemical Brightness of Various Portions of the Sun's Disk." By H. E. Roscoe (*Proc. Roy. Soc.*, 1862, **12**, 648).

‡ "On a Method of Meteorological Registration of the Chemical Action of Total Daylight." By H. E. Roscoe (*Phil. Trans.*, 1865, **155**, 605).

intensity as estimated by the eye, the action of the atmosphere being 17·4 times greater on the chemical than on the luminous rays when the sun's altitude is about 25°, and 26·4 times greater when it is 12°.*

With a view to the introduction of the instrument into meteorology, and as part of the routine work of an observatory, he caused a regular series of measurements to be made during two years at the Kew Observatory, under the direction of Dr. Balfour Stewart, and in order to gain further knowledge of the variation in the chemical action of light in different areas of the earth's surface he sent the writer of this notice, in 1866, to Pará, on the Amazon River, 1°28′ S. of the Equator. The Kew observations showed that the mean chemical intensity at hours equidistant from noon is practically the same on the same day, and that the daily maximum of chemical intensity corresponds to the maximum of solar altitude. Measurements showing the daily rise and fall of chemical intensity for each of the twenty-four months were obtained, as well as of the biennial variation for the same period. It was pointed out that the curve of yearly chemical intensity is not symmetrical about the vernal and autumnal equinoxes. Thus for 100 chemically active rays falling at the spring equinox at Kew there fell at the autumn equinox 167 rays, the sun's mean altitude being the same, the difference being probably due to the greater atmospheric opalescence in the spring.

The Pará observations were interesting from the fact that they were the first measurements of photometric intensity made within the tropics and that they served to dispel certain fallacies about photographic effects in very hot climates at that time current. The observations showed that the relation between the sun's altitude and chemical intensity may be represented by the equation

$$CI_a = CI_0 + \text{const. } a,$$

where CI_a represents the chemical intensity at a given altitude (a) in circular measure, CI_0 the chemical intensity at the altitude 0, and const. a a number to be calculated from the measurements. Comparisons between the observations at Kew and at Pará on the same days in April showed that the daily mean chemical intensity at the latter place was from ten to fifty times greater than at Kew, the wide difference being due to the enormous and rapid variations in intensity from hour to hour which the chemically active rays experience in the tropics during the rainy season of the year.†

* "Note on the Relative Chemical Intensities of Direct Sunlight and Diffuse Daylight at Different Altitudes of the Sun." By H. E. Roscoe and T. Baxendell (*Proc. Roy. Soc.*, 1867, **15**, 20).

† "On the Chemical Intensity of Total Daylight at Kew and Pará, 1865–1867." By H. E. Roscoe (*Phil. Trans.*, 1867, **157**, 555).

The relation between the sun's altitude and the chemical intensity of daylight was more accurately determined by the writer from a long series of observations made by Roscoe's method under a cloudless sky at Moita, near Lisbon, in the autumn of 1867. The fact was confirmed that direct sunlight is robbed of its chemically active rays at altitudes below 10°, and that although the chemical intensity for the same altitude at different places and at different times of the year varies according to the varying transparency of the atmosphere, yet the relation at the same place between altitude and intensity is always represented by a straight line. The differences in the observed actions for equal altitudes, which may amount to more than 100 per cent. at different places, and to nearly as much at the same place at different times of the year, serve as exact measurements of the varying transparency of the atmosphere. As illustrating the wide differences in the daily march of chemical intensity at various places, it was found that when light of unit intensity acting for twenty-four hours is taken as 1,000, the value of the mean chemical intensity at Kew is represented by the number 94·5, that at Lisbon by 110, and that at Pará by 313·3.*

Roscoe's hope that measurements of the chemical intensity of daylight might become part of the routine work of meteorological observatories has, unfortunately, not been realised. Measurements of the kind undoubtedly consume much time, and if properly conducted would require the whole service of a skilled assistant. But considering the enormously important part played by chemically active light in the economy of nature, and more particularly in the phenomena of vegetable life, it cannot be doubted that a sufficiently long-continued series of observations, systematically carried out on a well-considered plan at observatories distributed over the earth's surface, would afford most valuable information concerning the facts of solar energy, and incidentally serve to elucidate many important collateral questions. With the assistance of Mr. Horace Darwin, Roscoe made attempts to devise an automatic arrangement which should minimise the labour of observation, but in the absence of any assurance that such an instrument would be utilised trials with it were discontinued.†

On leaving Heidelberg to settle once more in London, Roscoe, as already stated, engaged Dittmar as research assistant, and they

* "On the Relation between the Sun's Altitude and the Chemical Intensity of Total Daylight in a Cloudless Sky." By H. E. Roscoe and T. E. Thorpe (*Phil. Trans.*, 1870, **160**, 209).

† "On a Self-recording Method of Measuring the Intensity of the Chemical Action of Total Daylight." By H. E. Roscoe (*Proc. Roy Soc.*, 1874, **22**, 158.

jointly studied by Bunsen's methods the absorption of hydrochloric acid and ammonia in water, proving that these gases do not obey Dalton and Henry's law.*

He next attacked, first with Dittmar's and then with Schorlemmer's assistance, the nature of aqueous solutions of the common volatile acids of constant boiling point, and showed that although the ratio of acid to water is constant for a definite boiling point under a particular pressure, this does not necessarily indicate the existence of definite hydrates. The composition of the hydrated acid on boiling is wholly dependent on the pressure, a concentrated solution losing acid and a dilute solution losing water until the residue in each case acquires a constant composition, not necessarily in simple molecular proportions, but depending on the pressure under which it is boiled.†

In those days Gmelin's "Handbuch," which the Cavendish Society had conveniently translated for us, was the chief repository of chemical knowledge—or the absence of it—and many suggestions as to possible fields of inquiry were to be gleaned from a study of its pages. One such subject was perchloric acid and its compounds, concerning which but little was then known beyond the nature and composition of potassium perchlorate as established by Count Stadion as far back as 1816. Roscoe made a fairly complete study of perchloric acid, its hydrates, and a number of its salts.‡

He narrowly escaped serious injury when working with ethyl perchlorate, first prepared, in 1840, by the American chemists Hare and Boye, and known to be extremely unstable. He was engaged in filtering a few cubic centimetres of this liquid when it exploded with great violence, a deep hole was bored into the base of the wooden filter-stand, and many hundreds of fragments of glass were driven into his hand. That filter-stand was long an object of interest to visitors to the private laboratory of the old Owens College in Quay Street.§

He also published a short note on thallium perchlorate, which had been prepared by the writer in a pure state, who determined its composition and established its isomorphism with the alkaline

* "On the Absorption of Hydrochloric Acid and Ammonia in Water." (*Journ. Chem. Soc.*, 1860, **12**, 128).

† "On the Composition of the Aqueous Acids of Constant Boiling Points." By H. E. Roscoe (*Journ. Chem. Soc.*, 1861, **13**, 146; 1862, **15**, 213.)

‡ "On Perchloric Acid and its Hydrates." By H. E. Roscoe (*Proc. Roy. Soc.*, 1861, **11**, 493).

§ "Note on Perchloric Ether." By H. E. Roscoe (*Journ. Chem. Soc.*, 1862, **15**, 213).

perchlorates, the crystallographic characters of which had been already ascertained by Kopp.*

Roscoe's most important contribution to inorganic chemistry was, without question, his well-known research on vanadium and its compounds, which occupied him for the greater part of five years. Some time in 1865 his attention was drawn to the occurrence of small quantities of vanadium in some of the copper-bearing beds of the Lower Keuper Sandstone of the Trias which were then being worked at Alderley Edge and Mottram St. Andrews, in Cheshire. He obtained possession of a large quantity of a lime precipitate, a waste product which was found to contain about 2 per cent. of vanadic acid. It was a most unpromising material, but eventually a method was worked out by which the vanadium was extracted as an ammonium vanadate; this, on heating, yielded an impure vanadic acid. Considerable difficulty was met with in freeing the vanadic acid from accompanying phosphoric acid, which clings to it with great tenacity and modifies its properties. Even small quantities of phosphoric acid cause the vanadic acid after fusion to solidify as a pitch-like, amorphous mass quite unlike pure vanadic acid.

It was the writer's privilege to assist in the early stages of this investigation, and it fell to his duty to carry out the various experiments which eventually served to establish the composition of the oxides of vanadium, the true nature of its volatile chloride, the existence of hitherto unknown oxychlorides, and of the mononitride which Berzelius had regarded as the metal, and, lastly, to fix its real atomic weight and to show that it was approximately 16 below that assumed by Berzelius on the mistaken supposition that vanadium compounds were analogous in composition to those of chromium.

It was only very gradually that the true chemical relationships of vanadium revealed themselves. For a time the indications were contradictory and perplexing. The first clue was given by Rammelsberg's observation that vanadinite is isomorphous with pyromorphite and mimetesite—two analogously constituted minerals containing phosphorus and arsenic. The next significant fact discovered was that by the action of a reducing agent it was possible to obtain a solution of a vanadium oxide which on reoxidation to vanadic acid appeared to require as much oxygen as Berzelius's vanadium, regarded as metal, would have needed. When it was ascertained that the volatile liquid chloride

* "On the Isomorphism of Thallium Perchlorate with the Potasium and Ammonium Perchlorates." By H. E. Roscoe (*Journ. Chem. Soc.*, 1866, **4**, 504).

which Berzelius had assumed was a trichloride, and free from oxygen, in reality contained oxygen, and was analogous in composition to phosphoryl chloride, the complication was rapidly cleared up, and the chemical relationships of vanadium to phosphorus, arsenic, and the other members of the trivalent group of the elements were established. This, of course, necessitated revising the formulæ of all vanadium compounds up to that time known. The previsions of Mendeléeff's great generalisation would, presumably, have indicated the place of vanadium in the scheme of the chemical elements. When the periodic law was actually promulgated a year or two later, vanadium had already taken up its true position.

Roscoe's first memoir on the subject was read to the Royal Society on December 19th, 1867, and was made the Bakerian Lecture of that session.*

On February 14th, 1868, he gave a Friday evening discourse at the Royal Institution "On Vanadium, one of the Trivalent Group of Elements," when the writer of this notice acted as his lecture-assistant. Having completed the arrangement of the lecture-table and set up the apparatus needed for the experimental illustrations, he occupied a spare half-hour in wandering through the old laboratories in the cellars of the Institution sacred to the genius and labours of Davy and Faraday. In looking over some specimens in a cupboard he came upon a small bottle containing ammonium vanadate labelled "Sent to me by Berzelius, 1831," and on it Faraday's well-known monogram by way of signature. A portion of the specimen was afterwards placed at Roscoe's disposal by Sir Edward Frankland, at that time Fullerian Professor of Chemistry. On examination it was found to contain considerable quantities of phosphoric acid, thus serving to indicate the probable cause of the discrepancy between the numbers obtained by Bunsen and by Roscoe on heating vanadic acid in hydrogen in the course of the observations required to determine the atomic weight of vanadium. It had been found that the presence of even traces of phosphorus prevents the complete reduction of vanadium pentoxide to vanadous oxide.

Part II. of "Researches on Vanadium," dealing with the chlorides VCl_4, VCl_3, and VCl_2, and metallic vanadium, which he obtained by heating the dichloride in hydrogen, was presented to the Royal Society on June 16th, 1869,† and his last memoir, treat-

* "Researches on Vanadium. Part I." By H. E. Roscoe (*Phil. Trans.*, 1868, **158**, 1.)

† "Researches on Vanadium. Part II." By H. E. Roscoe (*Phil. Trans.*, 1869, **159**, 679).

ing of the bromides and of certain of the metallic vanadates, including vanadinite, which he prepared artificially, on April 7th, 1870.*

With the mention of a short communication "On Two New Vanadium Minerals" (roscoelite and mottramite) to the *Proceedings of the Royal Society* for 1877,† and of a lecture on "Recent Discoveries about Vanadium" at the Royal Institution, the above statement includes all Roscoe's published contributions to the chemical history of vanadium. He handed over the further prosecution of the subject to his senior students, and, under his inspiration and direction, a considerable number of communications from the Owens College laboratory were made to the Chemical Society, namely, from Bedson (1876), Crow (1876), H. Baker (1878), Kay (1880), Brierley (1886), Hall (1887), and are published in the *Transactions*.

Other noteworthy contributions by Roscoe to inorganic chemistry are his study of tungsten compounds, in which he describes the existence of the pentachloride, WCl_5, and the corresponding pentabromide, WBr_5,‡ and his discovery of uranium pentachloride, UCl_5.§ These compounds are of theoretical interest on account of their "anomalous" character. He also discovered columbium trichloride, $CbCl_3$, which he found to have the remarkable property of decomposing carbon dioxide when heated in that gas, with the formation of columbium oxychloride, $CbOCl_3$, and carbon monoxide, a type of reaction not exhibited by any other metallic chloride.

He also determined the vapour densities of the chlorides of lead and thallium, which he showed to be normal.‖

An examination of the earth-metals contained in samarskite showed that the new metal announced by Delafontaine under the name of "philippium" was a mixture of yttrium and terbium.** The spark spectrum of terbium was at the same time mapped by him and Schuster. An examination of a specimen of oxide which

* "Researches on Vanadium. Part III." By H. E. Roscoe (*Phil. Trans.* 1870, **160**, 317).

† "On Two New Vanadium Minerals." By H. E. Roscoe (*Proc. Roy. Soc.*, 1877, **25**, 109).

‡ "A Study of Certain Tungsten Compounds." By H. E. Roscoe (*Manchester Lit. Phil. Soc. Proc.*, 1872, **11**, 79).

§ "On a New Chloride of Uranium." By H. E. Roscoe (*Journ. Chem. Soc.*, 1874, **12**, 933).

‖ "Note on the Specific Gravity of the Vapours of the Chlorides of Thallium and Lead." By H. E. Roscoe (*Proc. Roy. Soc.*, 1878, **27**, 426).

** "A Study of some of the Earth-metals contained in Samarskite." By H. E. Roscoe (T., 1882, **41**, 277).

ought to contain "philippium" in large quantities, should that element exist, showed no conclusive evidence of any other metals than yttrium or terbium.*

In 1882 he sent a note to the French Academy on a redetermination of the atomic weight of carbon by the method of Dumas and Stas, using Cape diamonds, and obtained the value 12·002 (O=16) as the mean of six experiments (A., 1882, 794). He also showed, with the assistance of Schuster, that the spectrum of carbon dioxide furnished by the South African diamond was identical with that furnished by other forms of carbon.

So long as he remained in Manchester Roscoe made occasional contributions to the meetings of the Philosophical Society of Manchester on subjects of general or local interest. Among them were: On arsenic eating in Styria; on a crystallised carbon compound in the Alais meteorite; on the amount of carbonic acid in Manchester air; on the corrosion of leaden hot-water cisterns; Dalton's first table of atomic weights—all of which are printed either in the *Proceedings* or *Memoirs* of the Society.

Roscoe was largely instrumental in making spectrum analysis and its initial results generally known in this country. Almost immediately after the publication of Bunsen and Kirchhoff's classical paper in *Poggendorf's Annalen*, he translated it for the *Philosophical Magazine*. He also proceeded to give public lectures on the subject, beginning with one at the Royal Institution on March 1st, 1861—perhaps the most successful, on account of the novelty and interest of his story, of the many he delivered there.

In 1868 he gave a course of six lectures before the Society of Apothecaries of London. These were afterwards published, with additions, in an admirably illustrated and eminently readable volume. It had a considerable measure of success, a second edition, still more largely augmented, being called for within a year. In the preparation of a third and fourth edition he was assisted by his friend, Dr. Schuster. As the successive editions show, the rate at which literature accumulated round the subject was altogether unprecedented in the history of scientific discovery.

Roscoe made an attempt to apply the spectroscope to the Bessemer process of steel manufacture, but he subsequently handed over the study of the peculiarities of the spectrum of the converter-flame to his former pupil and assistant, Dr. Marshall Watts.

Considering his interest in the subject, comparatively little original work on spectroscopy was published by Roscoe. In addition to the papers mentioned, he was concerned in the following:

* "The Spectrum of Terbium." By H. E. Roscoe and A. Schuster (T., 1882, **41**, 283).

"On the Effect of Increased Temperature upon the Nature of the Light Emitted by the Vapour of Certain Metals or Metallic Compounds." By H. E. Roscoe and R. B. Clifton (*Manchester Lit. Phil. Soc.*, 1860–1862, **2**, 227).

"Note on the Absorption-spectra of Potassium and Sodium at Low Temperatures." By H. E. Roscoe and A. Schuster (*Proc. Roy. Soc.*, 1874, **22, 362**).

"On the Absorption-spectra of Bromine and Iodine Monochloride." By H. E. Roscoe and T. E. Thorpe (*Phil. Trans.*, 1878, **167**, 207).

He formed one of the members of the Government Expedition sent to Sicily to observe the total solar eclipse of December 22nd, 1870, when the vessel conveying the party from Naples was wrecked off Aci Reale by striking a submerged and uncharted rock. Luckily no lives were lost, and the instruments were eventually got on shore. It was arranged that Roscoe, assisted by the late Sir George Darwin and Mr. Bowen, of Harrow School, should make observations on the spectrum of the corona from a position on Mount Etna as high as the snow would permit, but unfortunately during the minute of totality a violent hailstorm broke over the party, and no observations were possible. A number of measurements of the chemical intensity of daylight during the progress of the eclipse were made by the writer at Catania, some distance away, by the method described by Roscoe in the Bakerian Lecture for 1865. These showed that the diminution in the total chemical intensity of the sun's light during an eclipse is directly proportional to the magnitude of the obscuration of the solar disk.*

Roscoe's services to chemistry are to be measured as much by his contributions to its educational literature as by his efforts to enlarge its boundaries by original inquiry. His various text-books, ranging from "First Steps" through different grades to the most comprehensive treatise, have proved of the greatest service to the teacher, and have exercised a powerful influence in the diffusion of chemical knowledge in this kingdom and abroad. His "Lessons in Elementary Chemistry" was first published in 1866, and went through numerous editions, and despite the competition of dozens of similar works is still a favourite class-book. At the suggestion of Lothar Meyer it was translated into German by Schorlemmer and published by Vieweg, and has been largely used in German schools and colleges. Translations have appeared also in Russian, Italian, Hungarian, Polish, Swedish, in modern Greek, Japanese, and in one of the Indian vernaculars.

* "On the Measurement of the Chemical Intensity of Total Daylight made at Catania during the Solar Eclipse of 22nd December, 1870." By H. E. Roscoe and T. E. Thorpe (*Phil. Trans.*, 1871, **161**, 467).

Still more successful, as regards its sale, was his "Chemistry Primer," published in 1870, and intended to serve as the first step in chemistry in schools. It also was translated into Icelandic, Polish, German, Italian, Japanese, Bengali, Turkish, Malayalam, and Tamil.

He also published two text-books on "Inorganic Chemistry," one for beginners in conjunction with Dr. Lunt, and a larger one, for more advanced students, in association with Dr. Harden, each of which has reached a second edition.

A far more ambitious undertaking was the large "Treatise on Chemistry," in which he had the invaluable co-operation of his colleague Schorlemmer. The first volume of the work appeared in 1877. Its merits are too well known to need description. The inorganic section has passed through several editions, and has been revised from time to time with the help of many collaborators. The original edition was translated into German by Schorlemmer, and the book has largely replaced the time-honoured Graham-Otto as a text-book in colleges and technical schools. Unfortunately, owing to Schorlemmer's death in 1892, the organic section in the English edition was never finished. It has, however, been completed in the German edition under the direction of the late Professor Brühl—a circumstance which would seem to throw some light on the comparative position of the study of organic chemistry in this country and in Germany.

Roscoe undertook the editorship of the Century Series of Biographies of Scientific Men projected by Cassell and Co., to which he contributed a popular account of the life and work of Dalton—a little book written with much relish and a thorough appreciation of the fine character of its subject.

Some years after he had reached the allotted span he was induced to put together his reminiscences, and his Autobiography appeared in 1906. It is of interest as a record of a singularly full and varied life, and has historical value as the story of the educational changes, particularly in science, which he lived to witness or helped to secure. The book serves also to illustrate many features in its author's own character, and affords a pleasing picture of a singularly happy and successful life—of the life of one whom the Romans would have called "a man of good fortune," that is, of one whose prosperity was not the result of accident or chance, but of wisdom and the capacity to bring its aims and efforts to a successful ending.

Roscoe was elected into the Royal Society in 1863, and served on its Council from 1872 to 1877, and again during two subsequent periods, 1881–1883 and 1888–1890. He was a Vice-President in 1881–1882 and again in 1888–1890. As already stated, he gave

two of the Bakerian Lectures, and in 1873 was awarded a Royal Medal.

He joined the Chemical Society in 1855, and served on its Council in 1860–1864 and again in 1871–73. He was a Vice-President in 1873–1875, and again in 1877–1880, and was President in 1880–1882. His two Presidential Addresses—"abstracts and brief chronicles of the time"—dealt mainly with the results of chemical inquiry during the preceding year, especially in relation to the inorganic section of the science. No member of the Society ever showed himself a more beneficent or more generous friend. The walls of its rooms bear witness to his kindly thought and constant remembrance. Its Library has been augmented by gifts from him of close on a thousand volumes, including rare alchemical and early chemical works, and complete and handsomely bound sets of some of the most valuable serial publications of the science.

It was in grateful recognition of this warm-hearted encouragement of the Society and its objects that his old pupils resolved to commemorate his connexion with it by placing, on the occasion of his eightieth birthday, his bust in the Library he had so greatly enriched.

Roscoe was one of the original members of the Society of Chemical Industry, and took a leading part in establishing it on its present basis as a national institution with local sections in many of our principal towns and branches in certain of our Colonies and in America. He presided at the meeting in the rooms of the Chemical Society at which it was constituted, served as its first President, and was the first Chairman of its Manchester Section.

A significant proof of how the Society recognised its indebtedness to its first President and virtual founder was seen in the presentation to him of its Medal on the occasion of the Nottingham meeting in 1914.

In 1909 he was Honorary President of the Seventh International Congress of Applied Chemistry which met in London in that year. It was his wish that his friend, Dr. Ludwig Mond, as an eminent industrial chemist, should be appointed to that office, but Mond declined the position and proposed Roscoe's name instead at the preceding meeting in Rome.

To Roscoe, therefore, fell the honour of introducing the Prince and Princess of Wales—our present King and Queen—to the meeting of 3000 industrial chemists assembled in the Albert Hall, when the Prince welcomed the gathering in a felicitous speech. The foreign delegates were afterwards received in private audience by King Edward VII., when Roscoe, as Honorary President, had the honour of presenting them.

Roscoe's first introduction to the British Association was at

the Glasgow meeting in 1855, when he acted as Secretary of the Chemical Section. At this meeting he read a paper on the results of a joint investigation with Bunsen on the action of light on chlorine water, afterwards printed in the *Journal of the Chemical Society*. At the Manchester meeting of 1861, when, as already stated, he acted as one of the local secretaries, he presented a valuable report, jointly with Drs. Schunck and Angus Smith, on the condition of manufacturing chemistry in the South Lancashire district (*Brit. Assoc. Rep.*, 1861, 108). At the Bath meeting in 1864 he gave one of the evening lectures on the Chemical Action of Light. At the Liverpool meeting of 1870 he presided over the Chemistry Section. Unhappily, at that time, as now, France and Germany were at war. But, alas! neither the cosmopolitan character of science nor more than forty years of that brotherly intercourse among its votaries, which he so confidently hoped would "render impossible the breaking out of disasters so fatal to the progress of science and to the welfare of humanity," as he then witnessed, have served to avert an even more fearful disaster. The small but living fire which he then contended would in the end "surely serve to melt down national animosities" is well-nigh extinguished, and by the action of a nation which claims to be the most enlightened and most cultured of all nations.

In 1884 he again served as President of the Chemical Section at the meeting in Montreal. In 1887 he was President of the Association at the Manchester meeting in that year—an honour he prized all the more on account of his long association with that city. The meeting was notable as being the largest held since the foundation of the Association, and was remarkable for the number of foreign chemists present.

Roscoe continued to direct the Chemical Department of Owens College until his election as Member of Parliament for the Southern Division of Manchester in the autumn of 1885. On resigning his professorship the Council recorded its strong sense of the eminent services he had rendered to the College during a period of thirty years, and its conviction that to his attainments as a man of science, his skill and success as a teacher and organiser, his widespread reputation, and his high personal qualities it was in great measure due both that the College enjoyed so high a rank as a place of education, and that its chemistry department in particular had long held a position second to that of no other academic institution in the United Kingdom.

Similar testimony was borne by his colleagues when placing his portrait by Burgess in their Common Room, and by his pupils when offering another portrait by Herkomer to Lady Roscoe. In

a short account which Roscoe compiled and had printed for private circulation he recorded, with pardonable pride, the rise and progress of the chemical department of the Owens College during the thirty years he directed it; and he indicated the leading principles which had guided him in developing it. From the outset he was firmly convinced that the great blot in English industrial life was a singular want of appreciation of one of the essential conditions of success, namely, a sound training in the scientific principles which underlie all practice. That the practical result of working the Owens College chemical department in full recognition of this fact was satisfactory was proved by the steady increase in the number of his pupils, session after session, and the variety of responsible positions many of those pupils subsequently filled. When he laid down his office he could point to the fact that his laboratories, spacious as they were then thought to be, had been more than full during the previous half dozen years. It has been calculated that upwards of 2000 men had passed through them. No similar place in the kingdom could show such a record of contributions to chemical knowledge. From first to last it had furnished 235 original communications, mainly to the *Journal of the Chemical Society* and the *Proceedings* and *Transactions* of the Royal Society.

During his tenure of the Professorship of Chemistry at Owens College, Roscoe was called on to serve on two important Royal Commissions. The first was that on Noxious Vapours, which led to the amendment and extension of the Alkali Acts of 1891 and 1892. The second was the Commission on Technical Instruction in 1881—one of the most important and valuable Commissions ever issued when regard is had to its influence on the industrial welfare of this country. Roscoe threw himself heart and soul into its work, for he was profoundly convinced of its importance. During the ten years that succeeded the publication of its report he, in common with several of his colleagues, addressed innumerable public meetings in order to make its lessons known as widely as possible. All this labour bore fruit in the Technical Instruction Act of 1889, and still later, and to a fuller extent, in the Education Act of 1902—a measure preceded by Lord Bryce's Commission on Secondary Education, of which Roscoe was a member.

In spite of what had been accomplished, he was far from being satisfied with our national position. As late as 1906 he wrote: "Much remains for us in England to accomplish in the organisation of our secondary and scientific training, in which our competitors are before us, and of which the importance and the effects are well summed up in the following opinion of an eminent

German manufacturer: 'We in Germany do not care whether you in England are Free Traders or Protectionists, but what we are afraid of is that some day your people will wake up to the necessity of having a complete system of technical and scientific education, and then with your energetic population, with your insular position, and with your stores of raw material it will be difficult, or it may be impossible, for us to compete.'"

In 1884 a Knighthood was conferred on him, "in acknowledgment of his distinguished service on the Technical Education Commission."

Roscoe has recorded in his Autobiography the circumstances, altogether unexpected by him, which led to his introduction to active political life. In 1885 he was the only Liberal returned for a Manchester division. He kept his seat during two succeeding elections—1886 and 1892—but lost it in 1895 by a narrow majority. Although frequently solicited to re-enter the House of Commons, he felt, to use his own words, he "had had enough." During the greater part of his parliamentary career he sat on the Opposition benches, and had comparatively little opportunity of accomplishing any legislative achievements. On questions involving scientific matters he could always secure the ear of the House, especially when these related to the comfort and well-being of its members, as when he took in hand the ventilation, lighting, and drainage of the Palace of Westminster. In 1888 and again in 1889 he introduced a Technical Education Bill, but it failed to reach the Statute Book. In the latter year, however, the Government passed the Technical Instruction Act; this, although not wholly in accord with the views he had put forward, was gladly accepted by him as a satisfactory instalment. His effort to pass an Amending Bill in the following year met with no success. In 1891 the National Association for the Promotion of Technical Education, which was founded as the result of the Report of the Royal Commission of 1881, entrusted him with a Bill to remove certain disabilities in the working of the Act of 1889, and this he succeeded in carrying. In his last session he was Chairman of the Select Committee on Weights and Measures, which led to Mr. Balfour's Bill for legalising the use of the metrical system in this country. He was a Vice-President of the Decimal Association, and lost no opportunity of advocating the adoption of a system which nearly every other civilised community has found it expedient to employ.

The reform of the method of holding Parliamentary Elections, continuation schools; opening museums on Sundays; the housing of the science collections at South Kensington; grants to university colleges; industrial employment in Ireland; limitation of moisture

in weaving sheds; river pollution—were all questions on which he was able to exercise knowledge or influence, and most of which he lived to see satisfactorily settled.

Roscoe was long and honourably connected with the University of London. A graduate in 1853, he acted as an examiner in chemistry from 1874 to 1878. It was largely through his action that laboratory work was introduced into the curriculum in chemistry for science degrees. This not only greatly enhanced their value, but reacted beneficially on the general character of laboratory instruction throughout the country. On relinquishing Parliamentary work he became a member of the Senate, and in 1896 succeeded Sir Julian Goldsmid as Vice-Chancellor. It was during his term of office that the Act of 1898, which reconstituted the University, was passed. He had as Vice-President of the Association for promoting a Professorial (Teaching) University for London, of which Huxley was President, made proposals with the idea of uniting what have come to be called the Internal and External functions of the University, and in his evidence before Lord Cowper's Commission which preceded the Act of 1898 he suggested machinery of a less cumbrous and, as he hoped, of a more satisfactory character than that which became law. As Vice-Chancellor it became his duty to watch the progress of the measure, and to use his influence in promoting its passage, and his Autobiography reveals how actively he exerted himself to this end. The Statutory Commission, which followed the University of London Act of 1898, reported in 1900, its provisions were approved by Parliament in June of that year, and the new Senate held its first meeting in the following October. Roscoe took an active share in the rearrangements consequent on the reconstitution of the University, and in the changes necessitated by its removal from Burlington Gardens to the buildings of the Imperial Institute at South Kensington. Not the least of the services he thus rendered was his action with regard to the election of Sir Arthur Rücker as its first Principal. It was largely through his efforts that the appointment was made. Its success more than justified those efforts, and he always spoke of it as the best day's work he ever did for the University.

Roscoe resigned the Vice-Chancellorship in 1902, when he presented to the University the handsome mace which now lies on the table during the meetings of the Senate, and is used on ceremonial occasions. It was so employed, draped in crape, at the memorial service in Rosslyn Hill Chapel at his death.

He remained a member of the Senate until 1910, when age and increasing deafness necessitated his retirement. In the resolution

of condolence which the Senate passed at its first meeting after his death, they recalled with gratitude and admiration the great services he had rendered to the University during the twenty-one years of his membership of the Senate, first as Fellow and later as one of the representatives of His Majety in Council; and especially the wisdom, born of long experience in academic administration, with which he guided the University during the six years of his Vice-Chancellorship, which witnessed its reconstitution under the Act of 1898.

Roscoe was a Fellow of Eton College, as a representative of the Royal Society, from 1889 to 1912, and did what he could during the twenty-three years he served on the Governing Body to overcome what he terms "the enormous inertia of this ancient machine." He sought to further the teaching of physical science in the school by himself giving lectures, and through his efforts it is the richer by no less than one large and one small physical laboratory, a physics lecture-room, a workshop, and two more chemical laboratories, with store-rooms, etc. He also reorganised the system of teaching, and introduced graduated courses, which have resulted in an all-round improvement. Nevertheless, the results have not been commensurate with all the hard work and enthusiasm he put into his efforts. They have been largely discounted by factors over which he had no control. No one realised this more clearly than himself, and he felt keenly the disappointment of his hopes, so much so that more than once he considered the advisability of resigning his Fellowship as a protest. He earned the gratitude of the science staff by his uniform kindness and sympathy and by the readiness with which he would discuss their difficulties with them and help them with advice and encouragement.

As the representative of the Royal Society his chief interests lay with the teaching of physical science, but they did not rest there. No Fellow worked harder for the general welfare of the school. In order to make himself acquainted first-hand with facts connected with the subjects to be discussed at the meetings of the Provost and Fellows, he constantly visited Eton. His opinion and advice on all sorts of questions were sought and respected, and he has left behind him a record of whole-hearted service to the school that will long be remembered with appreciation and gratitude.

His wide experience as an educationist, and in particular his success in furthering the development of Owens College, naturally caused him to be consulted when institutions of a similar type were projected, and he was occasionally induced to take part in their government. Thus he had a large share in the arrangement of the curriculum of University College, Dundee, in 1881, and he was

afterwards concerned, as a member of the Scottish Universities Commission, in establishing the connexion of that College with the University of St. Andrews. He was appointed by the Duke of Devonshire to a governorship of University College, Liverpool, a position particularly gratifying to him as a member of a distinguished Liverpool family. He had a seat on the Council of Firth College, Sheffield, as a representative of the University of London, and was of service with respect to its science curriculum.

In 1888 he acted as a member of an Executive Commission appointed to carry out the provisions of the Scottish Universities Act. The Commission succeeded in devising ordinances which in many respects revolutionised the systems of the Scottish universities by providing new avenues to degrees, and thus, it may be hoped, affecting to an important extent the character of scientific education in Scotland.

In 1889 he was appointed a member of a Committee to act with the Commissioners of the 1851 Exhibition in drawing up a scheme for the establishment of research scholarships, and in 1896 he succeeded Lord Playfair as Chairman of the Scholarships Committee, and became a member of the Board of Management.

In 1901 he consented, on the invitation of Lord Elgin, the Chairman, to join the Executive Committee of the Trustees appointed to administer Mr. Carnegie's munificent gift to the Scottish universities for the benefit of scientific education, and he assisted in the inauguration of a system of Carnegie scholarships and fellowships for the encouragement of original investigation resembling that of the Royal Commissioners of the 1851 Exhibition.

Roscoe's high appreciation of Pasteur's early work as a chemist was, we may presume, the immediate cause of the interest with which he had followed his remarkable discoveries concerning the causes and cure of chicken cholera, anthrax, and the silk-worm disease—an interest quickened, no doubt, by the circumstance that he had made his personal acquaintance as far back as the early 'sixties. He had informed himself of the working of the Institut Pasteur in Paris, and with the details of the anti-rabic treatment, and had borne his share in combating the mischievous prejudices of those in this country who had sought to misrepresent the character and objects of Pasteur's work. In 1886 he had used his Parliamentary influence to induce Mr. Chamberlain, then President of the Local Government Board, to appoint a Government Commission consisting of Lord Lister, Sir James Paget, Professor Ray Lankester, and himself, with Sir Victor Horsley as secretary, to inquire and report on the efficacy of Pasteur's treatment of hydrophobia. They came to the conclusion, based on irrefragable

proof, that this treatment had saved a large number of lives that otherwise would have been sacrificed to a dreadful death. This report induced Sir James Whitehead, when Lord Mayor of London, to call a Mansion House meeting for the purpose of raising a fund with the double object of offering some acknowledgment of our indebtedness to Pasteur and his institute for having gratuitously treated some 200 of our countrymen, and of defraying the cost of sending poor persons who may need treatment to Paris. The Royal Society requested Roscoe with Sir James Paget and Professor Lankester to represent them at the meeting, and supported its object by a formal letter from the President. Roscoe, having occasion to respond for "Science" at a Royal Academy banquet, seized the opportunity again to direct attention to the subject, and he afterwards spoke in the House of Commons of the great value of experiments on living animals in opposition to an amendment designed to impede the working of the Vivisection Acts. By memorials, popular lectures, and articles in the periodical Press, he kept the subject continually before the public eye. Nor were his colleagues less active in instructing and forming public opinion. Their efforts eventually resulted in the establishment of an institute in London with aims similar to those of that in Paris. Thanks to the munificent generosity of Lord Iveagh, it has been housed and equipped not less worthily than its sister foundation in France. The London Institute of Preventive Medicine now bears the honoured name of Lord Lister, its first President. Roscoe was the first chairman of its governing body, and up to the last continued to take a keen and active interest in its beneficent work.

Roscoe's services to science and the cause of education were recognised all the world over. He was D.C.L. of Oxford and LL.D. of Cambridge, Dublin, Glasgow, and Montreal; D.Sc. of Aberdeen, Liverpool, and Victoria. On the occasion of the eighth jubilee of the foundation of Heidelberg University, he was made an honorary M.D. He was an Officer of the Legion of Honour, and a corresponding member of the French Institute of the Academy of Sciences. He was an honorary member of the American Philosophical Society of Philadelphia, of the New York Academy of Sciences; of the Chemical Society of Berlin; the Bunsen Gesellschaft; the Verein für Naturwissenschaft of Brunswick; the Physikalische Verein of Frankfort; a corresponding member of the Bavarian Academy of Sciences of Munich, and of the Royal Society of Sciences of Göttingen; the Reale Accademia dei Lincei, Rome; the Academy of Natural Sciences of Catania, Leop. Carol. Akad. of Halle, and of the Physiogr. Sällsk. of Lund. He was an honorary member of the Royal Irish Academy, and of the Literary

and Philosophical Society of Manchester. In 1912 the Franklin Institute awarded him the Elliott Cresson Medal.

He was sworn of the Privy Council in 1909—an honour which he regarded less as a personal distinction than as a recognition of the claims of science.

Of all the marks of honour and esteem he received in the course of his long and busy life, none gave him deeper and more heart-felt pleasure than that afforded by the action of his old pupils in celebrating the fiftieth anniversary of the day—March 25th, 1854—on which he took his Heidelberg degree. The warmth and cordiality with which the idea of commemorating this jubilee was everywhere received, not only by his students, but by every teaching institution, academic body, and scientific society with which he was or had been connected, were a striking testimony to the universal regard in which he was held. The celebration was fittingly held in the beautiful Whitworth Hall of the Victoria University in presence of a large and enthusiastic gathering of old students and former colleagues, and of friends who had journeyed specially to Manchester to present addresses. These literally came from all parts, and were accompanied by innumerable letters and messages from distinguished friends, chemists, and physicists throughout Europe, America, and the British Dominions beyond the Seas.

Of these addresses, he says in his Autobiography, that which touched him most nearly was the one from his former pupils. Offered to him in such a place, and in presence of so many familiar faces, it brought back to him some of the most cherished memories of his life. He touched on some of these in the course of his reply. His pupils had paid grateful homage to him; he in turn paid it to Bunsen and to those who had so loyally assisted him in building up the Manchester School of Chemistry.

In 1863 he married the lady whom he had first met, some ten years previously, in the house of his uncle, Mr. Justice Crompton-Lucy, the youngest daughter of Mr. Edmund Potter, M.P. for Carlisle, a well-known Manchester merchant, and a friend and co-worker of Cobden and Bright. She died in 1910. Of this union all that can be said here is: "Of the forty-seven years of married life, one who looked on can say there never were two more of one heart and mind." The one great sorrow of their lives was the death of their only son when an undergraduate at Oxford just when he was entering on manhood. He was a youth of much promise and of great charm of manner, and had already given evidence of considerable literary ability. Two daughters were also born of this marriage, the elder of whom is married to Mr. Charles

Mallet, formerly M.P. for Plymouth and Under Secretary for War in the late Liberal Government.

Time dealt tenderly with Roscoe. His vigorous, manly frame and healthy constitution seemed to defy the ravages of age. Except for increasing deafness and recurrent attacks of gout—a dispensation which he used ruefully to observe he had done nothing to deserve—his burden of years sat lightly on him. His happy temperament, no doubt, contributed to this alleviation. A singularly calm and equable disposition, habitual cheerfulness, a constant tendency to see and believe the best of things and of people, strong social instincts, a saving grace of humour, and a generous, impulsive hospitality—these characteristics through life were as strongly marked in him at fourscore years as at forty. On the evening of his death he was forming plans to celebrate his approaching birthday in the society of a chosen few of his old pupils. His mental activity never seemed to diminish. During the last years of his life much of it was exercised in efforts to avert, so far as in him lay, a catastrophe which he felt to be impending, and which, when it came, cast a shadow over the few months that were left to him.

He died at his Surrey home on the morning of December 18th, 1915. His end came wholly unexpectedly, swiftly, and almost painlessly; it was just such a passing as he would himself have wished. Happy through life, he was happy also in the manner of his death.

T. E. T.

HUGO SCHIFF.

BORN APRIL 26TH, 1834; DIED SEPTEMBER 8TH, 1915.*

As the result of a painful illness, borne with stoic fortitude, Hugo Schiff died at Florence on September 8th, 1915, at the age of eighty-one, after a strenuous life wholly devoted to the study and teaching of chemistry. During his long career he had witnessed the profound change and vigorous development which our science has undergone from 1850 to the present day. To this development he frequently contributed by his own labours, and he has left the lasting impress of his mind and of his activity on almost all branches of chemistry. He achieved deserved fame in the world of science, and the Chemical Society elected him an honorary and foreign member on June 16th, 1892.

Hugo Josef Schiff was born on April 26th, 1834, at Frankfort-on-Main, then a free town, and was the brother of the celebrated

* Translated from the author's Italian manuscript by G. B.

physiologist, Moritz Schiff. He completed his studies in the University of Göttingen, where Wöhler, then in the prime of life and at the height of his scientific activity, was the centre of an enthusiastic group of admirers and collaborators, some of whom afterwards became famous; among these were Limpricht, Beilstein, Fittig, and Kraut. He took his degree in philosophy at Göttingen on January 30th, 1857, with a thesis entitled, "Ueber einige Naphtyl- und Phenyl-derivate." Soon afterwards the young graduate had to emigrate to Switzerland on account of too liberal ideas, and for some time he taught as a Privatdozent in the University of Berne. Subsequently he came to Italy, and after a short stay at the University of Pisa, he was called to Florence by the well-known physicist, Carlo Matteucci, at that time Minister of Public Instruction. Schiff was appointed to teach chemistry in the Museo di Storia Naturale. In the "Elaboratorio" of this institution Torbern Bergmann and Felice Fontana had worked, and Humphry Davy, in March, 1814, had carried out some researches on iodine and repeated the experiments of Giuseppe Averani and of Cipriano Targioni on the combustion of diamond. In 1877 Schiff was appointed professor of general chemistry in the University of Turin, a post formerly held by Raffaele Piria. From Turin he returned in 1879 to Florence in order to occupy the chair of general chemistry in the Istituto di Studi superiori. He did not move again, and it was largely owing to his efforts that the Florentine Chemical Laboratory was transformed and organised in such a way that it could bear comparison with the best institutes of its kind. At Florence, when already more than fifty years of age, he married a lady of great charm and refinement, Signora Ida Merzbacher (*née* Feistmann), but he had no children.

In the laboratories at Turin and Florence, as in his younger days at Berne, he was always a persevering and indefatigable worker, and brought numerous experimental investigations to a successful conclusion. Schiff's was a versatile mind, and he was equally at home in organic and inorganic, as well as in physical and biological chemistry. His first work on naphthyl and phenyl derivatives was followed by studies on metal-ammonium compounds, mostly carried out at Berne, by work on the specific gravity of solutions, and later by important investigations on the cinnamic series, which supplement those of Bertagnini and of Perkin. He also carried out extensive researches on the constitution of many natural glucosides, such as amygdalin, arbutin, populin, helicin, æsculin, and phloridzin. He did important work on aldehydes and their derivatives, in connexion with which he introduced the magenta–sulphurous acid solution, commonly known as "Schiff's reagent."

The nature and constitution of the compounds formed by aldehydes with amines, the so-called "Schiff's bases," were explained by him. We may further note his work on colour-bases derived from furfuraldehyde, at first thought to belong to the type of malachite-green, but shown by more recent work to have a different structure (*Ber.*, 1905, **38**, 3824). This investigation led to the discovery of the extremely sensitive xylidine–acetic acid reagent for furfuraldehyde. We must further record his studies on the dilatation of solutions of ammonium salts, on the esters of boric acid, and numerous publications on a variety of subjects belonging to inorganic chemistry. He was one of the first to attack the difficult question of the constitution of tannins, and although his contribution to this important problem may not have led to definite results, perhaps because the time was not yet ripe, it nevertheless opened the way to the recent masterly researches of E. Fischer. Further studies of interest to biologists are those on the biuret reaction and the separation of the acidic from the aminic function of amino-acids. His work on condensation products from aspartic acid must be counted among the first attempts to obtain polypeptide substances of high molecular weight possessing some of the properties of the proteins.

A sagacious investigator, he intuitively saw what subjects of research were important. Although later investigations have sometimes modified his conclusions, nevertheless the merit is his of having successfully attacked, with characteristic skill, problems which were always attractive and often in advance of his time. A resourceful experimentalist, he often succeeded in surmounting or avoiding difficulties by original and inexpensive means. We owe to him many simple and practical pieces of apparatus now in common use. It is sufficient to mention the nitrometer which bears his name, and the apparatus for purifying oxygen and air for organic analysis. He was endowed with a wonderful memory, and had a complete mastery of old and modern literature of various branches of science; at a moment's notice he could quote name, date, and results with certainty and precision. He also had a considerable knowledge of mathematics. In 1876 Schiff published his "Introduzione allo Studio della Chimica," which was translated into several languages and contained many ideas remarkable for the period. This originality is also shown in some articles written by him for the "Enciclopedia di Chimica" by F. Selmi. In 1871 he founded with Cannizzaro and Selmi the *Gazzetta chimica italiana*.

Schiff was trained in a school which cherished the glorious traditions of Berzelius and Wöhler. He modelled his own teaching, both

in lecture-room and laboratory, on the methods of these great masters, and developed a strong critical faculty in his pupils, whilst at the same time he knew how to arouse in them enthusiasm and pleasure in experimental work. After the premature death of Piria (1813–1865) and that of Bertagnini (1827–1857), the teaching of chemistry in Italy had been revived by the schools of Cannizzaro and of Selmi. Schiff also soon collected around him an appreciative school, from which there went forth competent academic and technical chemists over the whole of Italy, as well as into foreign countries; some of these now occupy important university chairs, others are at the head of considerable industrial undertakings. In 1909 when the age limit for university teachers was fixed in Italy at seventy-five years, Hugo Schiff was among the few who were allowed to retain their chairs on account of special merit.

In addition to his purely professional attainments, Schiff had a vast store of literary, linguistic, and historical knowledge, which made him a brilliant and amusing conversationalist. He had marked predilection for classical and humanistic learning, and gladly would he have written over the door of his students' laboratory the words which Plato is said to have wished graven over the entrance to the Academy: Μηδεὶς ἀμαθὴς εἰσίτω μοῦ τὴν στέγην * This wide culture and his special inclination for historical research was used to advantage in his studies on the history of chemistry. We may mention here his discriminating essay entitled, "Il teologo e filosofo Giuseppe Priestley e la pneumatologia," and a publication, "L'Università degli Studi di Firenze," printed in 1887. The latter is justly valued as a fine example of historical criticism.

A severe, original, occasionally bizarre personality made Hugo Schiff exacting in the execution of duty, both to himself and to others. One might imagine that he had taken as his motto the words of Carlyle: "The strong man will ever find *work*, which means difficulty, pain, to the full measure of his strength." His devotion to science was intense, and he not infrequently allowed his brother Moritz to conduct physiological experiments on his person. Whilst not eager of gain, he practised the strictest economy, and his pursuit of science was always wholly disinterested. When in April, 1904, preparations were made, with the co-operation of chemists from all over Europe, to celebrate his seventieth birthday, it was characteristic of the man that he should insist on the ceremony being a simple one. To the sum of several thousand lire collected by his pupils and admirers, he added a larger sum himself, for the foundation of a biennial prize in chemistry. Vanity and outward pomp were foreign to his nature, and one of his last

* Let none who loves not learning enter here.

wishes was that his funeral should be absolutely simple, in the early morning, without flowers or mourners.

His liberal and democratic ideas, which in his youth made him take an active part in political and social movements, were the cause of his having to leave Germany and emigrate to Switzerland, as already mentioned. In later life, whilst still preserving a keen sympathy for democratic ideas, he remained aloof from political action. For close on twenty years he lived a life of seclusion, giving all his energies to the laboratory and to teaching. But he was not insensitive to the hopes and fears of his contemporaries, nor was he a selfish recluse. Only those who have been associated with him in daily work, and had the honour and good fortune of sharing with him through long years the ups and downs of success and disappointment which are inseparable from experimental research, only those who had thus been able to penetrate beneath a rugged and forbidding exterior, knew that while remaining true to his scientific materialism, this stern and austere man continued to cherish the most gentle ideals.

In spite of the weight of years and much ill-health, he continued to deliver his lectures to within a few weeks of his death, and until the last days of his life he kept in touch with scientific progress. But at last age and disease claimed their toll, and the end was perhaps hastened by grief at seeing the humanitarian ideals to which he had given the best of his youth, dissipated by a cruel war. It seems that his death was a painless one. On the morning of September 8th, after long weeks of suffering, he awoke, and turning his face towards the dawn he passed quietly away. Ἐν θνήσκοις.

M. Betti.

OTTO NIKOLAUS WITT.

Born March 31st, 1853; Died March 22nd, 1915.

Professor Otto N. Witt, of Charlottenburg, Fellow of the Chemical Society since 1876, died suddenly from heart disease on March 22nd, 1915.

By this premature and unexpected death chemical science loses one of her most distinguished representatives, Germany one of her best and most successful teachers of applied chemistry.

Otto Nikolaus Witt was born at St. Petersburg on March 31st, 1853. His father, a native of Holstein, held there the position of professor of general and applied chemistry at the Superior Technical School; his mother, Elisabeth Zwerner, was the daughter of a German who

had migrated to Russia and married a Russian lady. In 1864 Witt's parents left Russia, spent two years at Munich, and in 1866 settled at Zurich, where they assumed Swiss nationality. Witt was therefore a Swiss citizen until 1891, when, being appointed professor at Charlottenburg, he became by this fact a Prussian subject.

At Zurich, Witt was first a pupil at the "Gymnasium," and afterwards at the "Industrial School." In October, 1871, he entered the chemical section of the "Eidgenössische Polytechnische Schule," where Wislicenus, Emile Kopp, Victor Meyer, and Wilhelm Weith were teaching chemistry with brilliant success. At the "Industrial School" Witt had been familiarised with the elements of this science, so that, under the direction of the above-named excellent masters, he made rapid progress. In the autumn of 1873 he was appointed analytical chemist at the Vulken Iron Works at Duisburg, where he remained about six months. In the early part of 1874 he entered the printing works of Gabriel Schiesser at Hardt, near Zurich, where he had an opportunity of learning the application of the natural and artificial colouring matters in dyeing and printing, and could also in his free time do some scientific research work. Desirous of making more extensive researches and of obtaining the Ph.D. degree, he returned in the autumn of 1874 to the Polytechnikum, and in July, 1875, he presented to the Zurich University an "inaugural dissertation" on "Derivatives of Metadichlorobenzene" and on "Aromatic Nitrosoamines." In the autumn of 1875 he went to England, hoping to find there an appointment as chemist, like many other Continental men of science, and he entered shortly afterwards the colour works of Williams, Thomas and Dower, at Brentford, near London.

In January, 1876, he discovered chrysoidine, a brilliant orange, basic azo-colouring matter, and soon afterwards a series of acid azo-colours, which were put on the market under the name of tropæolines. At the same time, Roussin, in France, discovered also, quite independently, colours of the same class, which were manufactured by Poirrier, in Paris. Chrysoidine and Poirrier's oranges, the composition and mode of preparation of which were published in 1877 by A. W. Hofmann, and the tropæolines, were together with Manchester brown, the first technically important representatives of the class of azo-colouring matters which has since become of such enormous industrial value.

At Brentford, Witt devoted himself, not only to the study of the azo-colours, but worked also on the safranine and induline groups, and invented tolylene-blue and red, first members of the azine group, to which he afterwards made numerous contributions.

In 1876, a few months after entering the Brentford works, while still not yet twenty-three years old, he published his famous paper "On the Relation between the Chemical Constitution and the Colour of Organic Compounds," which is the base of the chromophore and auxochrome theory of colouring matters, now universally accepted.

In the latter part of 1879 he left England, and lived for some months at Frankfort-on-the-Main, where he worked at the factory of Messrs. Leopold Cassella & Co.; from there he moved to Mulhouse (Alsace) to carry out scientific and industrial researches in the laboratory of the "Ecole de Chimie," where he also gave a course of lectures on applied chemistry.

In 1882 he was offered a position as director of the "Verein Chemischer Fabriken" at Waldhof, near Mannheim, and superintended there the manufacture of colouring matters and scientific researches in this field.

Three years afterwards he resolved to leave industry and to devote himself entirely to the teaching of chemical technology. He attached himself to the Higher Technical School at Charlottenburg as "Privatdocent" in 1886, was appointed "Docent" for the application of colouring matters in 1888, and in 1891, when Rudolf Weber, the professor of chemical technology, retired from his chair, he became his successor.

During twenty-four years he held this position in the most brilliant and distinguished manner; his teaching of applied chemistry was certainly the best and the most complete in the world.

Witt's scientific activity extends over a period of more than forty years, his first paper being published in 1874, the last in 1915. One hundred and eight papers have been printed in the *Berichte* of the "Deutsche Chemische Gesellschaft," dealing with various branches of organic and even inorganic chemistry, and being most important contributions, especially to the chemistry of colouring matters.

Besides this scientific work, he carried out a great many industrial researches which have not been published. He was also the author of a very important book on the technology of textile fibres, bleaching, dyeing, and printing, which is not quite finished. He published most interesting contributions to the history of the development of chemical industry in recent years, and was an authority on patent law. Several pamphlets which he published were most appreciated by chemists as well as by lawyers.

He had a remarkable ability in explaining chemical features or problems, and was often requested to deliver lectures before scientific societies, both in Germany and in foreign countries, for instance, at the international chemical congresses at Berlin, Rome,

and London. The Berlin Congress, which had been organised and was presided over by him, was very successful, and gave much satisfaction to all who attended it.

Witt was not only an excellent chemist, but was also thoroughly acquainted with all other branches of natural philosophy, and had an extensive literary knowledge. He spoke and wrote perfect English and French, and was personally acquainted with most of the eminent scientific men of these two as well as of other countries.

He was thus well qualified to act as member of the jury at international exhibitions, and both at Chicago in 1893 and at Paris in 1900 he performed this function in a very satisfactory way.

He was also an able microscopist, and had devoted himself in the earlier part of his life to the study of the *Diatomaceae* with great success.

Photography had always been with him a favourite occupation in his free time; he was not only a successful amateur, but he did also some interesting scientific work in this field.

For many years he was the editor of *Die Chemische Industrie*, the great chemico-technical German paper.

In England, science has been popularised by the lectures and books of eminent men of science, such as Faraday, Huxley, Roscoe, Crookes, and others, and a paper, *Nature*, which had been started for this purpose, is widely read in all English-speaking countries. Wishing to give his countrymen something of the same kind, Witt founded in 1890 *Prometheus*, which he edited until 1912, and made many valuable contributions to it. The most interesting of them have been published in three separate volumes under the title "Narthekion."

E. Noelting.

CECIL HAMERSLEY WALDRON.

Born August 14th, 1885; Killed in Action, March 2nd, 1916

Lieutenant Cecil Hamersley Waldron, 7th Lincolnshire Regt., was born in 1885, and was the eldest son of Captain C. Waldron (late R.E.).

He was educated at Wilson's Grammar School, Camberwell, and afterwards at the Mathematical School, Rochester, whence he matriculated at the University of London in January, 1902, and in June of that year gained the School Leaving Exhibition awarded to the best scholar of the year. Pursuing his studies at the Cambridge Tutorial and Birkbeck Colleges, he passed the Inter.B.Sc. in 1903, and soon after was appointed assistant analyst to the

Vinolia firm, two years later taking up an important post in the head offices of the well-known firm of Messrs. Burroughs Wellcome and Co. He was elected a Fellow of the Chemical Society in 1912.

He delighted in travel, and spent several holidays on the Continent, including Russia, having made a close study of the Russian language.

When the war broke out, Mr. Waldron joined the University of London O.T.C., and was gazetted 2nd Lieut. in the 7th Lincolns, being promoted Lieutenant in January, 1915. He went to the front in July, and was killed in action, near Ypres, on March 2nd last, when leading his company (of which he had just been given the command) to the attack after forty-eight hours' most severe fighting. His commanding officer characterised him as one of his most valued officers, and states that his loss is keenly felt throughout the regiment.

Lieut. Waldron was a fine scholar, of a manly, generous nature, and, like so many others, sacrificed a most promising career at the call of his country's need.

SIR ANDREW NOBLE, Bart., K.C.B.

Born September 13th, 1831; Died October 22nd, 1915.

Sir Andrew Noble, Bart., was born at Greenock on September 13th, 1831; his father was an officer in the Royal Navy. He was educated at the Edinburgh Academy and at the Royal Military College, Woolwich. In his eighteenth year he obtained a commission in the Royal Artillery, and after serving abroad for some years, he was appointed secretary to the Royal Artillery Institute; in 1858 he became secretary to the Special Committee on Rifled Cannon, and later he was appointed to a similar position to the Committee on Plates and Guns. In 1859 he became assistant inspector of artillery, and in the following year began his membership of the Ordnance Select Committee, of which he remained an active member for some forty years. The work of these special committees brought Captain Noble in contact with Sir William Armstrong, who at that time was engaged in perfecting his rifled gun, and thus it came about that in 1860 Captain Noble became a partner in the Elswick Company, Newcastle-upon-Tyne. Thus began that association with the Elswick works which extended over more than fifty years. This period witnessed the growth of the Elswick firm, a growth which is surely unique amongst indus-

trial enterprises. This firm is at the present time represented by the great ordnance factory, the shipbuilding yards of Elswick and Walker-on-Tyne, and in addition to these developments on Tyneside it embraces the establishment in Manchester of the, at one time, rival firm of Sir Joseph Whitworth and Co. How much of this growth was due to the enthusiasm, the indomitable energy, the ceaseless and untiring work of Sir Andrew Noble we can only surmise, firmly convinced that his knowledge and his scientific researches have greatly contributed to the advancement in all its many departments of the Armstrong, Whitworth Company.

Sir Andrew Noble's scientific work has been of a character which has profoundly influenced the design of modern artillery. In 1862 he invented the chronoscope to determine the velocity of a projectile in a gun-barrel. In 1868 began that association and collaboration with the late Sir Frederick Abel which resulted in the publication of those classical researches, to which we owe our present-day exact knowledge of the phenomena and changes attending the firing of gunpowder, and of the nature of the gaseous and solid products formed. In like manner, the phenomena attending the burning of cordite have been the subject of much scientific work by Sir Andrew Noble, from which information of great practical importance resulted.

Captain Noble was made a Companion of the Bath in 1881, a Knight Commander in 1893, and was created a Baronet in 1902, and had many foreign Orders conferred on him. He was elected a Fellow of the Royal Society in 1870, and in 1880 was awarded the Gold Medal of that Society. On the occasion of the annual meeting of the Society of Chemical Industry in Newcastle in 1908 he received the Gold Medal of that Society; in 1909 he was awarded the Albert Medal of the Royal Society of Arts. The Universities of Oxford and Cambridge conferred on him the degree of Doctor of Science, and the University of Durham conferred the degree of Doctor of Civil Law. In 1908 he was elected an honorary member of the Institute of Civil Engineers; since the year 1869 he had been a Fellow of the Chemical Society.

On the occasion of the jubilee of his association with the Elswick works the Freedom of the City and County of Newcastle-on-Tyne was conferred on him. In 1915 Sir Andrew Noble was president of the North-East Coast Engineers and Shipbuilders, and was chairman of the Explosives Section of the International Congress of Chemistry at its meeting in London. It naturally fell to his lot to fill many public positions, and for many years Sir Andrew Noble was a Deputy-Lieutenant of Northumberland, and in 1896 was High Sheriff for the County.

A few years before his retirement from active participation in the work of the Armstrong, Whitworth Company, Sir Andrew Noble had purchased the estate of Ardkinglass, Argyllshire, where he erected a mansion, and it was here that he died on October 22nd, 1915, in his eighty-fifth year. Thus closed the career of one whose incomparable energy, ability, and creative genius achieved so much for science and industry, and, as recent events have so abundantly shown, has proved so invaluable an asset to his country. He is survived by Lady Noble, four sons and two daughters, and Major George John William Noble, late of the 13th Hussars, succeeds to the title.

P. P. B.

XXXVI.—*The Study of Binary Mixtures. Part II. The Densities and Viscosities of Mixtures containing Substituted Phenols.*

By Arthur Bramley.

In a former communication (this vol., p. 10) an account was given of a number of experiments that had been made on the densities and viscosities of some binary mixtures containing phenol. The results of these experiments support the view generally held that if the formation of a compound takes place between the two components of a binary mixture, the viscosities of the mixtures will be greater than the calculated means. The maximum difference between the observed and calculated viscosity was not found, as might have been expected, with the mixture which contains the two components in equimolecular proportions, but with a mixture the composition of which varied with the temperature. In some cases the viscosities were less than the calculated means, although the components of these mixtures are known to combine with each other.

One reason advanced for these anomalies was that one component of the mixture contained associated molecules when in the liquid state. The experiments about to be described were made in order to ascertain whether molecular association is the main cause of these abnormal viscosity curves.

Two methods are available for testing this point. First, by using a series of phenols which differ only in the degree of molecular association, and secondly, by ascertaining whether, on employing phenols in which the degree of molecular association is negligibly small, the anomalies mentioned above disappear. It is almost

impossible, however, to obtain phenols which satisfy these conditions, since they are all associated to a greater or less degree in the liquid state, and the introduction of substituent groups invariably alters other properties, such as acidity and salt-forming power, as well as the association factor. It is possible, nevertheless, by a judicious selection of substituted phenols, to obtain definite information in the direction desired.

The molecular association factors of several substituted phenols have been determined by Hewitt and Winmill (T., 1907, **91**, 441), who used the surface-tension method. They found that the degree of molecular association of the cresols was influenced by the position of the methyl group, and Boyd, who has recently determined the dissociation constants for the cresols (T., 1915, **107**, 1538), found that the introduction of the methyl group into phenol weakens the acidic property somewhat, and this again to an extent which depends on the position of the methyl group. This naturally will influence the extent of the formation of compounds when the cresol is mixed with a base such as pyridine. It so happens, however, that the effect of the methyl group on the dissociation factor will not be to mask the effect of the association factor on the shape of the viscosity curve, but rather to accentuate it. Mixtures of the three cresols and pyridine were therefore examined.

According to Hewitt and Winmill's measurements (*loc. cit.*), the presence of a chloro- or a nitro-group in the ortho-position in phenol reduces the association factor to zero, and since the acidic nature of *o*-chlorophenol and *o*-nitrophenol is much stronger than it is in phenol itself, it appeared that these two phenols, on account of the extensive formation of compounds that might be expected and the large diminution, if not complete elimination, of the effect of molecular association when mixed with such bases as those used in the experiments described in the previous communication (*loc. cit.*), should give results approaching what might be termed normal viscosity curves, and provide a means of testing, by the second method mentioned above, whether the peculiarities found in the viscosity curves for mixtures containing phenol are caused by the molecular association of the phenolic component. It was decided, therefore, to examine mixtures of *o*-chlorophenol and *o*-nitrophenol with several of the bases used in the experiments with phenol.

Experimental.

The determinations of densities and viscosities were made in the same way as described in Part I. (*loc. cit.*).

The three cresols used were purified, first by distillation, then by

freezing out, and finally by distillation again immediately before use.

The *o*-chlorophenol was prepared by the direct chlorination of phenol maintained at a temperature of 150—180°. The mixture of *o*-chlorophenol and *p*-chlorophenol, together with a little dichlorophenol and some unchanged phenol thus produced, was separated first by fractional distillation. The fraction of lower boiling point, which contained the *o*-chlorophenol and unchanged phenol, was subjected to further purification by freezing out. The latter method of purification is necessary, as it is almost impossible to effect a satisfactory separation of *o*-chlorophenol from unchanged phenol by distillation alone on account of the closeness of the boiling points of these two substances. The *o*-chlorophenol prepared in this way boiled constantly at 175° and solidified completely at 8°.

The *o*-nitrophenol used was purified by distillation under about 5 mm. pressure.

The other substances used in the experiments about to be described were purified in the same way as described in Part I.

The results obtained for mixtures of pyridine and *o*-cresol are given in tables I and I*a*; for mixtures of pyridine and *m*-cresol in tables II, II*a*, and II*b*; and for mixtures of pyridine and *p*-cresol in tables III, III*a*, and III*b*. The viscosity–composition curves for these three mixtures are shown in Figs. 1 2, and 3 respectively. The broken-line curves show the connexion between density and composition for a temperature of 20°. The density–composition curves for other temperatures run very approximately parallel to these.

TABLE I.

Mixtures of o-Cresol and Pyridine.

Weight per cent. of *o*-cresol	Densities.							
	0°	10°	20°	30°	40°	60°	80°	110°
0·00	1·0013	0·9916	0·9819	0·9723	0·9627	0·9424	0·9218	0·8900
12·05	1·0100	1·0005	0·9912	0·9818	0·9722	0·9531	0·9340	0·9040
24·55	1·0197	1·0104	1·0012	0·9928	0·9835	0·9653	0·9472	0·9178
33·60	1·0267	1·0178	1·0091	1·0005	0·9918	0·9742	0·9565	0·9276
45·83	1·0364	1·0279	1·0196	1·0112	1·0026	0·9855	0·9684	0·9403
55·91	1·0438	1·0355	1·0273	1·0190	1·0105	0·9937	0·9767	0·9490
66·83	1·0514	1·0430	1·0348	1·0265	1·0180	1·0013	0·9846	0·9570
77·73	1·0574	1·0491	1·0408	1·0324	1·0238	1·0070	0·9901	0·9623
85·72	1·0606	1·0522	1·0439	1·0356	1·0270	1·0099	0·9929	0·9649
91·85	1·0629	1·0545	1·0461	1·0376	1·0290	1·0117	0·9946	0·9664
100·00	1·0654	1·0568	1·0483	1·0399	1·0312	1·0137	0·9963	0·9678

FIG. 1.

o-Cresol and pyridine.

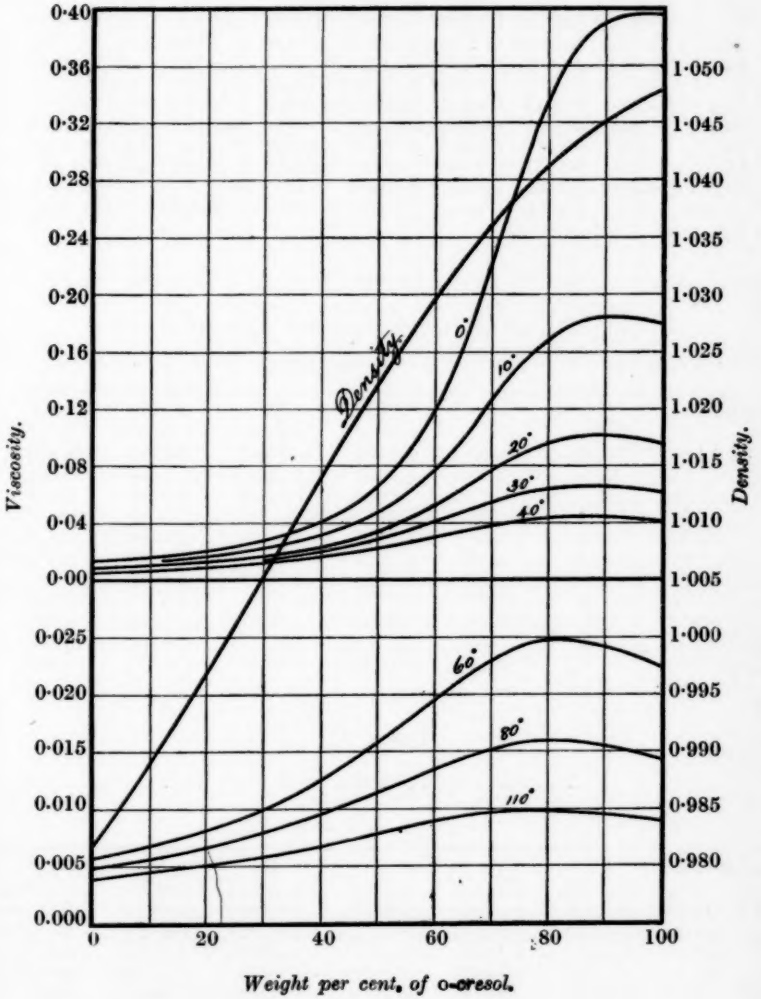


Table Ia.

Mixtures of o-Cresol and Pyridine.

Weight per cent. *o*-cresol	Viscosities							
	0°	10°	20°	30°	40°	60°	80°	110°
0·00	0·01323	0·01108	0·00941	0·00821	0·00714	0·00578	0·00487	0·00385
12·05	0·01669	0·01396	0·01176	0·01022	0·00886	0·00703	0·00577	0·00451
24·55	0·02335	0·01900	0·01556	0·01350	0·01148	0·00889	0·00720	0·00543
33·60	0·03155	0·0249	0·01983	0·01724	0·01436	0·01069	0·00852	0·00615
45·83	0·05315	0·0391	0·02962	0·02560	0·02045	0·01425	0·01060	0·00732
55·91	0·0936	0·0631	0·04455	0·03625	0·02750	0·01784	0·01253	0·00834
66·83	0·1824	0·1068	0·06845	0·04935	0·03575	0·02181	0·01467	0·00945
77·73	0·3152	0·1614	0·0926	0·06230	0·04290	0·02460	0·01586	0·00980
85·72	0·3770	0·1811	0·1004	0·06565	0·04415	0·02460	0·01573	0·00969
91·85	0·3925	0·1837	0·1001	0·06450	0·04325	0·02395	0·01528	0·00942
100·00	0·3970	0·1790	0·0956	0·06125	0·04100	0·02240	0·01431	0·00897

Table II.

Mixtures of m*-Cresol and Pyridine.*

Weight per cent. of *m*-cresol	Densities.					
	0°	10°	20°	30°	40°	60°
0·00	1·0013	0·9916	0·9819	0·9723	0·9627	0·9424
14·09	1·0098	1·0003	0·9908	0·9813	0·9718	0·9527
27·45	1·0181	1·0088	0·9995	0·9902	0·9809	0·9630
41·40	1·0264	1·0175	1·0086	0·9998	0·9909	0·9737
46·92	1·0296	1·0209	1·0121	1·0033	0·9946	0·9778
55·33	1·0345	1·0260	1·0174	1·0089	1·0003	0·9839
61·80	1·0377	1·0294	1·0211	1·0128	1·0045	0·9882
70·62	1·0418	1·0336	1·0254	1·0172	1·0089	0·9930
75·90	1·0439	1·0357	1·0275	1·0193	1·0110	0·9951
85·17	1·0467	1·0385	1·0303	1·0221	1·0139	0·9981
91·41	1·0479	1·0399	1·0318	1·0237	1·0155	0·9997
100·00	1·0493	1·0413	1·0333	1·0253	1·0173	1·0015

Table IIa.

Mixtures of m*-Cresol and Pyridine.*

Weight per cent. of *m*-cresol.	Viscosities.					
	0°	10°	20°	30°	40°	60°
0·00	0·01323	0·01108	0·00941	0·00821	0·00714	0·00578
14·09	0·01791	0·01466	0·01228	0·01098	0·00931	0·00731
27·45	0·02643	0·02105	0·01770	0·01461	0·01240	0·00949
41·40	0·0428	0·0325	0·02540	0·02125	0·01732	0·01267
46·92	0·0554	0·04015	0·03085	0·0251	0·02022	0·01419
55·33	0·0878	0·05935	0·0425	0·0335	0·02605	0·01755
61·80	0·1283	0·0804	0·05585	0·04175	0·03150	0·02019
70·62	0·2205	0·1285	0·0816	0·0557	0·03995	0·02425
75·90	0·3095	0·1664	0·0998	0·0652	0·04565	0·02619
85·17	0·500	0·2370	0·1308	0·07885	0·05255	0·02850
91·41	0·642	0·2855	0·1481	0·0864	0·05590	0·02955
100·00	0·844	0·3460	0·1690	0·0947	0·05925	0·02995

FIG. 2.

m-Cresol and Pyridine.

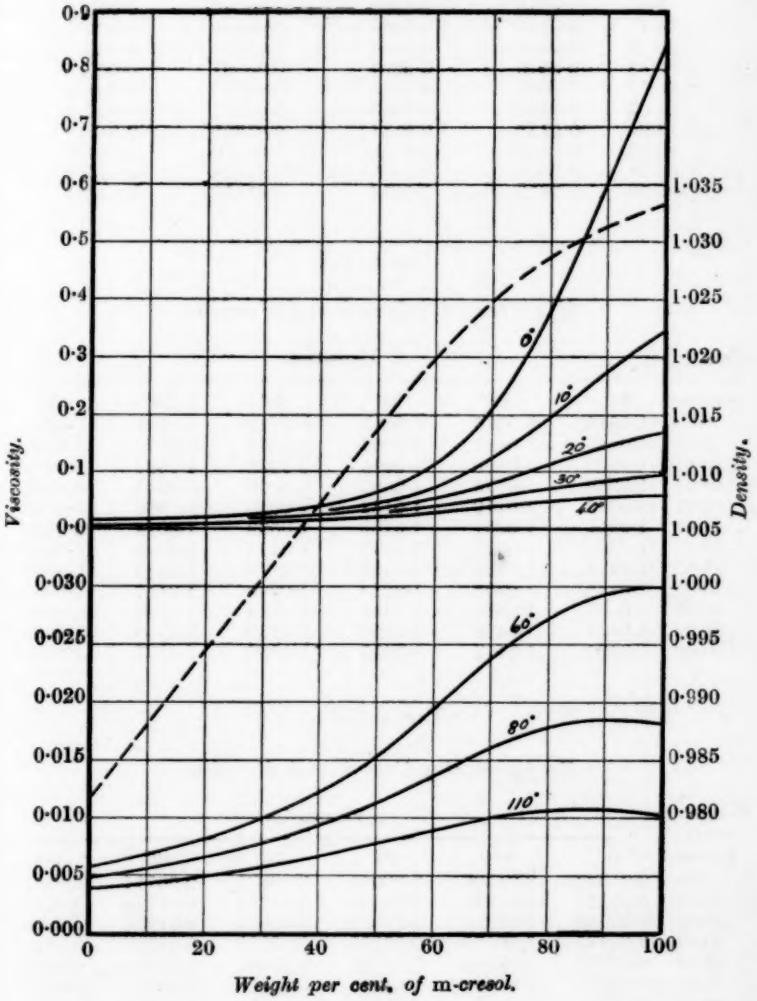


Table II*b*.

Mixtures of m-*Cresol and Pyridine.*

Weight per cent. of *m*-cresol.	Densities.		Viscosities.	
	80°	110°	80°	110°
0·00	0·9218	0·8900	0·00487	0·00385
14·47	0·9343	0·9036	0·00599	0·00457
26·75	0·9447	0·9154	0·00731	0·00539
38·43	0·9545	0·9264	0·00901	0·00646
50·72	0·9644	0·9375	0·01147	0·00775
61·52	0·9721	0·9455	0·01407	0·00910
70·94	0·9772	0·9511	0·01629	0·01010
82·33	0·9817	0·9555	0·01820	0·01074
90·88	0·9836	0·9576	0·01848	0·01052
100·00	0·9853	0·9594	0·01808	0·01023

Table III.

Mixtures of p-*Cresol and Pyridine.*

Weight per per cent. *p*-cresol	Densities.					
	0°	10°	20°	30°	40°	60°
0·00	1·0013	0·9916	0·9819	0·9723	0·9627	0·9424
21·03	1·0145	1·0051	0·9957	0·9865	0·9773	0·9592
29·61	1·0200	1·0108	1·0016	0·9926	0·9836	0·9661
40·04	1·0265	1·0176	1·0087	1·0000	0·9913	0·9744
46·71	1·0305	1·0219	1·0132	1·0046	0·9962	0·9795
54·46	1·0351	1·0267	1·0182	1·0099	1·0014	0·9850
60·37	1·0385	1·0302	1·0217	1·0133	1·0048	0·9888
67·82	1·0419	1·0338	1·0254	1·0170	1·0086	0·9927
75·36	1·0445	1·0365	1·0283	1·0200	1·0117	0·9959
83·28	1·0464	1·0386	1·0306	1·0223	1·0140	0·9984
91·01	1·0477	1·0400	1·0320	1·0239	1·0159	1·0005
100·00	1·0487	1·0412	1·0335	1·0257	1·0177	1·0026

Table III*a*.

Mixtures of p-*Cresol and Pyridine.*

Weight per cent. of *p*-cresol	Viscosities.					
	0°	10°	20°	30°	40°	60°
0·00	0·01323	0·01108	0·00941	0·00821	0·00714	0·00578
21·03	0·02178	0·01837	0·01451	0·01363	0·01139	0·00827
29·61	0·02792	0·02251	0·01808	0·01628	0·01370	0·00995
40·04	0·04165	0·03175	0·02535	0·02115	0·01727	0·01245
46·71	0·05795	0·04205	0·03105	0·02565	0·02065	0·01462
54·46	0·0867	0·0599	0·04215	0·0331	0·02600	0·01773
60·37	0·1241	0·0787	0·05315	0·0408	0·03115	0·02020
67·82	0·1908	0·1140	0·07365	0·05265	0·03830	0·02348
75·36	0·3120	0·1675	0·1004	0·06635	0·0466	0·02705
83·28	0·4985	0·2395	0·1324	0·0797	0·05415	0·02970
91·01	0·724	0·3113	0·1616	0·0926	0·0602	0·0315
100·00	0·984	0·3965	0·1895	0·1054	0·0654	0·0328

FIG. 3.

p-Cresol and pyridine.

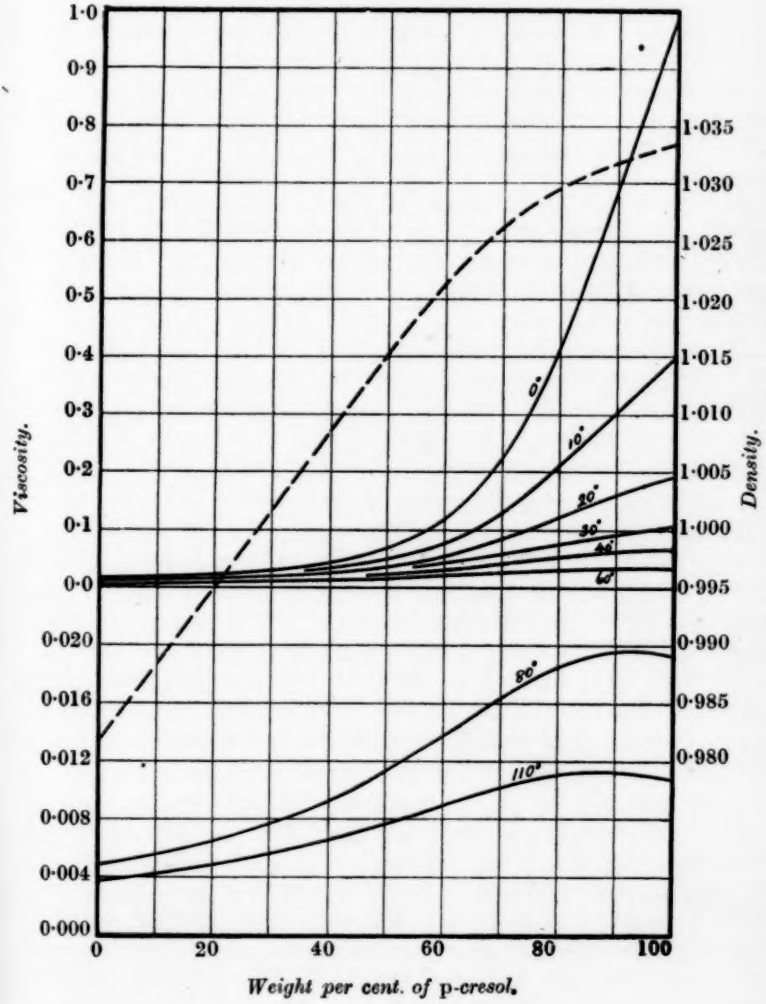


TABLE III*b*.

Mixtures of p-*Cresol and Pyridine.*

Weight per cent. of *p*-cresol.	Densities.		Viscosities.	
	80°	110°	80°	110°
0·00	0·9218	0·8900	0·00487	0·00385
14·06	0·9343	0·9037	0·00603	0·004605
27·48	0·9462	0·9165	0·00747	0·005515
41·10	0·9575	0·9291	0·00955	0·006765
54·03	0·9679	0·9410	0·01230	0·008225
63·11	0·9741	0·9474	0·01463	0·00940
71·88	0·9792	0·9527	0·01696	0·01047
81·72	0·9828	0·9566	0·01890	0·01120
89·95	0·9850	0·9588	0·01961	0·01111
100·00	0·9868	0·9604	0·01937	0·01081

A comparison of the results obtained for mixtures of the three cresols and phenol with pyridine shows clearly that there is a marked difference between the viscosity curves for the mixtures containing *o*-cresol and for those which contain *m*- and *p*-cresols and phenol.

It has been shown recently by Boyd (*loc. cit.*) that the acidity of phenol is reduced by the introduction of alkyl groups, and that the effect is most marked when the alkyl group is in the ortho-position with respect to the hydroxyl group. There is good reason to suppose, therefore, that in the four mixtures mentioned above the formation of compounds will be most extensive in the phenol–pyridine mixture and least in the *o*-cresol–pyridine mixture. The shape of the viscosity curves suggests, *ceteris paribus*, that the *o*-cresol–pyridine mixture contains more compound than the corresponding mixtures containing *m*- and *p*-cresols and phenol. Since this is not the case, there must be some other reason.

There is every indication, therefore, that the dominating factor which is the cause of this marked difference between the viscosity curves in the four cases under consideration is molecular association. This will be evident from the following table:

		Phenol.	*o*-Cresol.	*m*-Cresol.	*p*-Cresol.
Viscosities	0°	—	0·3970	0·844	0·984
	10	0·2010	0·1790	0·346	0·3965
	20	0·1104	0·0956	0·1690	0·1895
	30	0·0709	0·06125	0·0947	0·1054
	40	0·0474	0·0410	0·05925	0·0654
	60	0·0252	0·0224	0·02995	0·0328
	80	0·01580	0·01431	0·01808	0·01937
	110	0·00941	0·00897	0·01023	0·01081
Association factor		1·30	1·09	1·41	1·44
Temperature at which maximum on viscosity curves of mixtures with pyridine first appears.		45°	3°	67°	74°
Dissociation constant at 25°.		$1·15 \times 10^{-10}$	$0·63 \times 10^{-10}$	$0·98 \times 10^{-10}$	$0·67 \times 10^{-10}$

In the foregoing table the association factors are taken from Hewitt and Winmill's paper (*loc. cit.*), and the dissociation constants are the values given by Boyd (*loc. cit.*). The temperatures given in the last horizontal row but one have been obtained by interpolation from the figures recorded in the respective tables.

It is clear from the figures in the foregoing tables that the viscosities of the pure cresols and phenol, although by no means proportional to the association factors of these substances, are nevertheless in the same order throughout the whole range of temperature studied. There is no point of inflexion on the viscosity–composition curves for mixtures of pyridine with *m*- and *p*-cresols for the temperatures 0° and 10°, and it is only just evident at 20°. The temperatures at which a maximum on the viscosity–composition curve first makes its appearance are again in the same order as the association factors.

Care has been taken to point out in the foregoing paragraphs that there is less compound present in the mixtures of pyridine and *o*-cresol than in the corresponding mixtures containing the other cresols and phenol. It is necessary to take this into account, because a similar difference in the shape of the viscosity–composition curves can be obtained by varying this very factor. The following example will illustrate this: The amount of compound formed in a mixture of *m*-cresol and aniline will be greater than in a corresponding mixture of *m*-cresol and dimethylaniline on account of the weaker salt-forming character of the latter of these two bases. The disturbing influence of the molecular association of the *m*-cresol is the same in these two cases, so that any difference in the character of the viscosity curves for these two mixtures must result from the larger proportion of compound in the mixtures containing aniline.

Tsakalotos (*Bull. Soc. chim.*, 1908, [iv], **3**, 234) has measured the viscosities of mixtures of aniline and *m*-cresol, and his results show that the viscosity–composition curves for mixtures of these two substances are S-shaped, with maximum points near the *m*-cresol end of the curves; they resemble the *o*-cresol–pyridine curves. Kremann, Gugl, and Meingast (*Monatsh.*, 1914, **35**, 1365) measured the viscosities of mixtures of *m*-cresol and dimethylaniline, and found that at 9° the viscosity–composition curve contains no point of inflexion; it is convex towards the axis of composition throughout its length. At 64° an S-shaped curve was obtained, and at 77° the curve was similar, but the point of inflection had shifted considerably towards the dimethylaniline end of the curve. These curves resemble those for mixtures of *m*- or *p*-cresol and pyridine. Thus we have exactly the same kind of relationship between the viscosity curves for mixtures of *m*-cresol with aniline and with

dimethylaniline as there is between those for mixtures of *o*-cresol and pyridine and *m*- or *p*-cresol and pyridine, but the difference in the two cases is the result of unlike causes.

It seems reasonable, from such considerations as the above, to draw the conclusion that molecular association is a cause of high viscosity, and, if present in only one component of a binary mixture such as those under discussion, where partial chemical combination takes place, it may cause the viscosity–composition curve to have an abnormal shape, and minimise, or even mask altogether, some particular characteristic which the curve might otherwise possess.

Reference was made in Part I. to the unequal thermal dissociation of the molecular complexes of the associated component and of the compound formed in the case of mixtures of phenol and pyridine. These remarks are equally applicable to the mixtures of pyridine with the three cresols.

The foregoing experiments prove definitely that molecular association in one of the components of a binary mixture is a disturbing factor in the study of viscosity. If, therefore, this source of disturbance is eliminated, the viscosity curves should assume a more normal form. The association factor of *o*-chlorophenol is, according to Hewitt and Winmill's measurements, unity. If this deduction be true, the substitution of *o*-chlorophenol for phenol should result in a considerable simplification of the problem. There is a further advantage in the stronger acidic nature of *o*-chlorophenol, which should on that account yield a larger proportion of compound when mixed with a base, as a consequence of which, any peculiarity of the viscosity–composition curve which is characteristic of compound formation should be enhanced.

Mixtures of *o*-chlorophenol with the five bases—aniline, dimethylaniline, diphenylmethylamine, quinoline, and pyridine—were examined. In every case measurements were made over a considerable range of temperature. The results obtained are given in tables IV to VIII, and the viscosity–composition curves are shown in Figs. 4 to 8. The density–composition curve is given for one temperature only, namely, 20°. This shows that there is a considerable contraction in volume on mixing these two substances. No density curves are given for the other mixtures, as they are so nearly linear that they would appear as straight lines if drawn on such a scale as to come within the compass of the figures showing the viscosity curves. A few details regarding the density curves for these mixtures may be interesting.

The density–composition curves for mixtures of *o*-chlorophenol and aniline are so near linearity as to be almost indistinguishable from straight lines even when drawn on a large scale; those for mixtures of *o*-chlorophenol and dimethylaniline are slightly below

the linear, as are those for mixtures of *o*-chlorophenol and diphenylmethylamine also. The density–composition curves for mixtures of *o*-chlorophenol and pyridine are slightly sinuous, falling just below the straight line for mixtures rich in pyridine and lying a little above it for mixtures rich in *o*-chlorophenol.

The small curves inset in the various figures show, as before, the position of maximum deviation of the observed viscosity from the calculated mean and the corresponding temperature.

TABLE IV.

Mixtures of o-Chlorophenol and Aniline.

Weight per cent. of *o*-chlorophenol.	Densities.							
	10°	20°	30°	40°	60°	80°	110°	150°
0·00	1·0350	1·0218	1·0131	1·0045	0·9872	0·9700	0·9430	0·9052
15·54	1·0644	1·0555	1·0466	1·0377	1·0197	1·0017	0·9739	0·9354
28·94	1·0957	1·0865	1·0773	1·0681	1·0496	1·0311	1·0019	0·9620
40·16	1·1220	1·1124	1·1028	1·0932	1·0740	1·0548	1·0248	0·9839
46·61	1·1375	1·1278	1·1181	1·1084	1·0889	1·0694	1·0389	0·9972
51·68	1·1496	1·1397	1·1298	1·1199	1·1001	1·0803	1·0493	1·0069
56·87	1·1617	1·1517	1·1417	1·1317	1·1117	1·0917	1·0604	1·0177
60·61	1·1703	1·1602	1·1501	1·1400	1·1197	1·0994	1·0679	1·0249
65·18	1·1811	1·1709	1·1607	1·1505	1·1301	1·1097	1·0775	1·0339
68·50	1·1893	1·1790	1·1687	1·1584	1·1377	1·1170	1·0844	1·0404
77·80	1·2107	1·2002	1·1897	1·1792	1·1582	1·1372	1·1039	1·0590
89·65	1·2384	1·2275	1·2166	1·2057	1·1839	1·1621	1·1281	1·0823
100·00	1·2626	1·2512	1·2399	1·2284	1·2060	1·1834	1·1490	1·1028

TABLE IV*a*.

Mixtures of o-Chlorophenol and Aniline.

Weight per cent. of *o*-chlorophenol.	Viscosities.							
	10°	20°	30°	40°	60°	80°	110°	150°
0·00	0·0630	0·0428	0·03145	0·02405	0·01543	0·01100	0·00709	0·00446
15·54	0·09035	0·0578	0·0405	0·02945	0·01790	0·01222	0·00781	0·00498
28·94	0·1315	0·0774	0·0506	0·0354	0·02015	0·01327	0·00842	0·00539
40·16	0·1786	0·0960	0·0593	0·0399	0·02195	0·01407	0·00886	0·00568
46·61	0·2045	0·1056	0·0639	0·0420	0·02275	0·01443	0·00901	0·00577
51·68	0·2240	0·1124	0·0672	0·0433	0·02325	0·01462	0·00909	0·00582
56·87	0·2365	0·1166	0·0693	0·0439	0·0235	0·01470	0·00912	0·00585
60·61	0·2395	0·1176	0·0695	0·0440	0·0235	0·01470	0·00912	0·00585
65·18	0·2353	0·1148	0·0686	0·0434	0·0234	0·01460	0·00907	0·00584
68·50	0·2248	0·1096	0·0670	0·0424	0·0232	0·01444	0·00901	0·00581
77·80	0·1755	0·0904	0·0580	0·0379	0·02145	0·01368	0·00873	0·00572
89·65	0·1118	0·0630	0·0431	0·0301	0·01825	0·01222	0·00820	0·00559
100·00	0·0639	0·0421	0·0308	0·0232	0·01513	0·01070	0·00760	0·00546

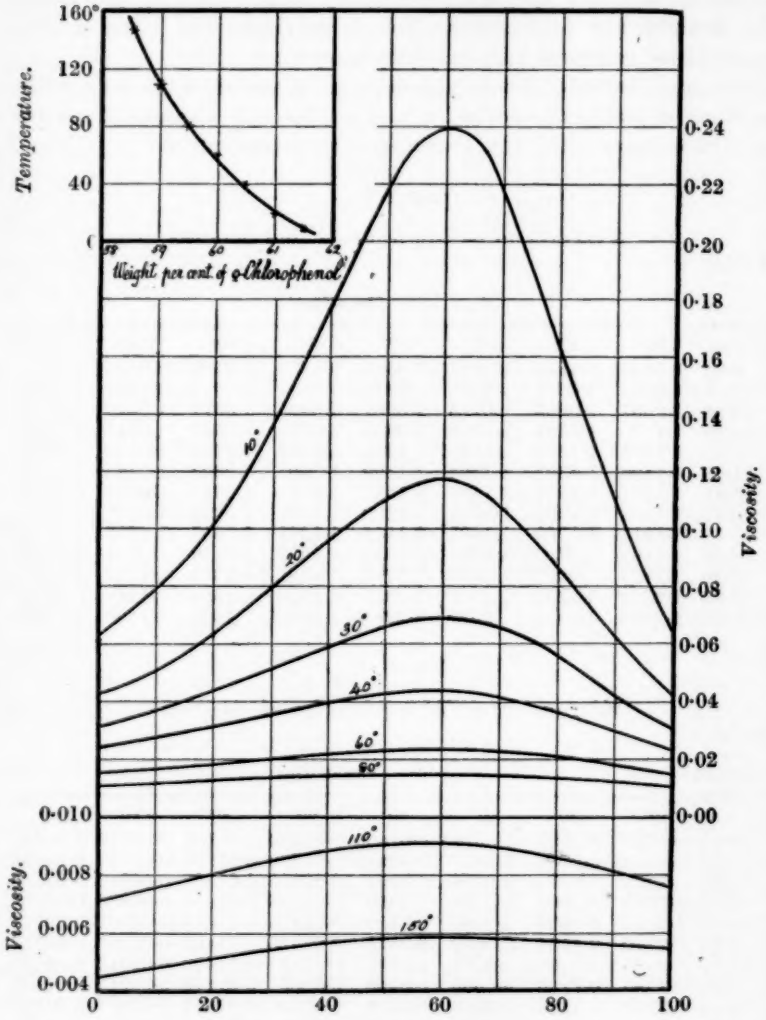
TABLE IV*b*.

Mixtures of o-Chlorophenol and Aniline.

Weight per cent. of *o*-chlorophenol	61·5	61·0	60·5	60·5	60·0	59·5	59·0	58·5
Temperature	10°	20°	30°	40°	60°	80°	110°	150°

FIG. 4.

o-Chlorophenol and aniline.



It should be mentioned in connexion with the results enumerated in the foregoing tables that Thole, Dunstan, and Mussell (T., 1913, **103**, 1114) measured the viscosities of mixtures of aniline and *o*-chlorophenol at 25° and 50°, but there is a discrepancy of several per cent. between the values of the viscosity of pure *o*-chlorophenol

given by them and those found by interpolation for the same temperatures from the author's figures.

The *o*-chlorophenol used throughout the experiments now being described was very carefully purified by the processes already mentioned. Several determinations of the viscosity were made at 20°, and the extreme values obtained, using different viscometers, were 0·0420 and 0·0422. The values found by the author for the densities of this substance at various temperatures agree well with those given by Hewitt and Winmill (*loc. cit.*). Repeated purification, both by redistillation and freezing out, failed to produce any alteration in either the viscosity or density.

TABLE V.

Mixtures of o-Chlorophenol and Dimethylaniline.

Weight per cent. of *o*-chloro-phenol.	Densities.						
	0°	10°	20°	30°	40°	60°	80°
0·00	0·9726	0·9644	0·9562	0·9484	0·9399	0·9235	0·9069
14·67	1·0070	0·9983	0·9896	0·9809	0·9722	0·9548	0·9374
27·71	1·0432	1·0341	1·0250	1·0159	1·0068	0·9887	0·9706
40·65	1·0820	1·0725	1·0630	1·0535	1·0440	1·0251	1·0062
52·49	1·1192	1·1093	1·0994	1·0895	1·0796	1·0600	1·0404
60·40	1·1444	1·1343	1·1242	1·1141	1·1040	1·0840	1·0640
70·50	1·1763	1·1659	1·1555	1·1451	1·1347	1·1142	1·0937
75·41	1·1930	1·1824	1·1718	1·1612	1·1506	1·1296	1·1086
80·87	1·2110	1·2002	1·1894	1·1786	1·1678	1·1465	1·1252
83·81	1·2207	1·2098	1·1989	1·1880	1·1771	1·1556	1·1341
90·14	1·2416	1·2305	1·2194	1·2083	1·1972	1·1754	1·1536
100·00	1·2741	1·2626	1·2512	1·2399	1·2284	1·2060	1·1834

TABLE V*a*.

Mixtures of o-Chlorophenol and Dimethylaniline.

Weight per cent. of *o*-clhoro-phenol.	Viscosities.						
	0°	10°	20°	30°	40°	60°	80°
0·00	0·02025	0·01655	0·01385	0·01170	0·01024	0·00798	0·00658
14·67	0·03020	0·02340	0·01859	0·01473	0·01243	0·00940	0·00731
27·71	0·0435	0·03135	0·02430	0·01890	0·01410	0·01078	0·00804
40·65	0·0676	0·0430	0·0305	0·0235	0·01660	0·01210	0·00878
52·49	0·0984	0·0568	0·0370	0·0279	0·01915	0·01338	0·00949
60·40	0·1190	0·0672	0·0414	0·0309	0·02085	0·01422	0·00995
70·50	0·1440	0·0796	0·0469	0·0341	0·02305	0·01524	0·01050
75·41	0·1540	0·0830	0·0489	0·03505	0·0240	0·01563	0·01072
80·87	0·1583	0·0844	0·0500	0·03545	0·0247	0·01589	0·01090
83·81	0·1572	0·0842	0·0498	0·03545	0·02475	0·01593	0·01097
90·14	0·1452	0·0800	0·0474	0·0341	0·0245	0·01578	0·01095
100·00	0·1079	0·0639	0·0421	0·0308	0·0232	0·01513	0·01070

TABLE V*b*.

Mixtures of o-Chlorophenol and Dimethylaniline.

Weight per cent. of *o*-chlorophenol.....	79·0	77·5	76·5	76·0	75·5	75·0	74·5
Temperature	0°	10°	20°	30°	40°	60°	80°

FIG. 5.

o-Chlorophenol and dimethylaniline.

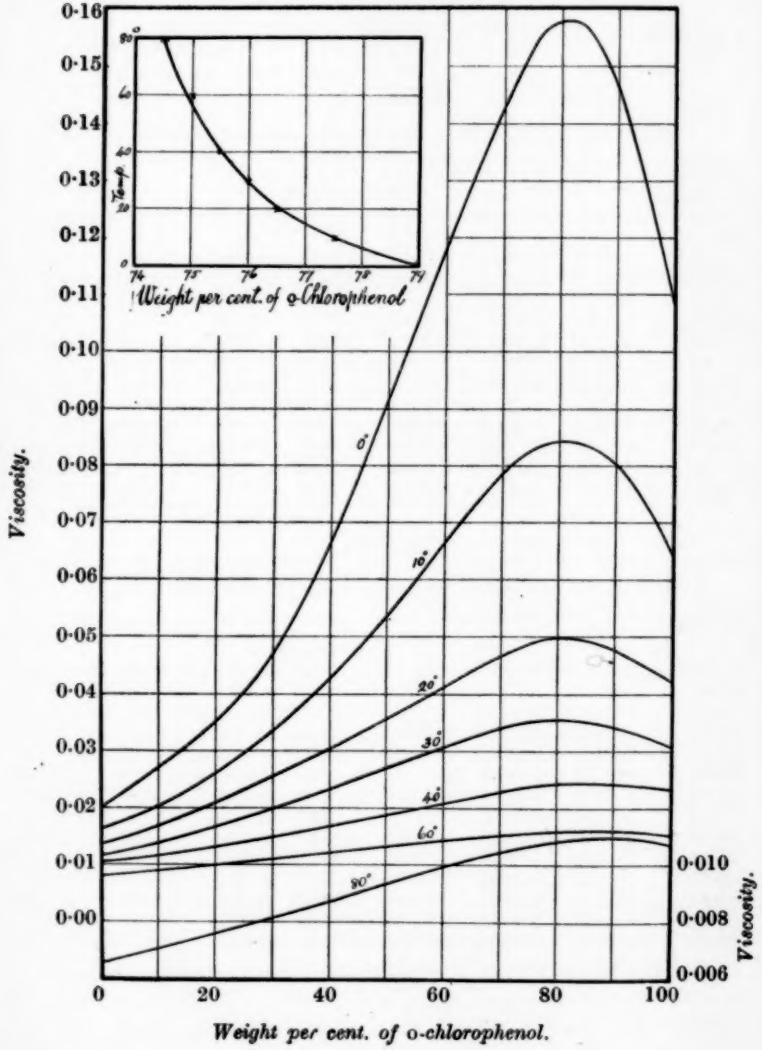


Table VI

Mixtures of o-Chlorophenol and Diphenylmethylamine.

Weight per cent. of *o*-chloro-phenol.	Densities.						
	0°	10°	20°	30°	40°	60°	80°
0·00	1·0675	1·0596	1·0518	1·0439	1·0360	1·0202	1·0044
13·83	1·0924	1·0842	1·0760	1·0678	1·0596	1·0432	1·0268
25·90	1·1147	1·1061	1·0975	1·0889	1·0803	1·0632	1·0461
38·35	1·1392	1·1302	1·1212	1·1122	1·1032	1·0853	1·0674
50·52	1·1639	1·1545	1·1451	1·1357	1·1263	1·1077	1·0891
57·58	1·1790	1·1692	1·1594	1·1496	1·1398	1·1204	1·1010
68·76	1·2032	1·1930	1·1828	1·1726	1·1624	1·1422	1·1220
79·34	1·2263	1·2157	1·2051	1·1945	1·1839	1·1630	1·1421
89·62	1·2494	1·2384	1·2274	1·2164	1·2054	1·1837	1·1620
100·00	1·2741	1·2626	1·2512	1·2399	1·2284	1·2060	1·1834

Table VI*a*.

Mixtures of o-Chlorophenol and Diphenylmethylamine.

Weight per cent. of *o*-chloro-phenol.	Viscosities.						
	0°	10°	20°	30°	40°	60°	80°
0·00	0·1835	0·1095	0·0725	0·0513	0·0384	0·0248	0·01735
13·83	0·1618	0·0985	0·0647	0·04635	0·0350	0·02275	0·01591
25·90	0·1459	0·0908	0·0595	0·04305	0·0325	0·02110	0·01500
38·35	0·1332	0·0845	0·0553	0·0403	0·0304	0·01965	0·01420
50·52	0·1250	0·0795	0·0520	0·03805	0·0285	0·01850	0·01347
57·58	0·1216	0·0767	0·0502	0·03685	0·0275	0·01795	0·01300
68·76	0·1169	0·0730	0·0479	0·0351	0·0260	0·01710	0·01238
79·34	0·1132	0·0699	0·0459	0·0336	0·0249	0·01638	0·01180
89·62	0·1103	0·0668	0·0440	0·03215	0·0239	0·01575	0·01120
100·00	0·1079	0·0639	0·0421	0·0308	0·0232	0·01513	0·01070

Table VII.

Mixtures of o-Chlorophenol and Quinoline.

Weight per cent. of *o*-chloro-phenol.	Densities.								
	0°	10°	20°	30°	40°	60°	80°	110°	150°
0·00	1·1078	1·1002	1·0926	1·0850	1·0773	1·0615	1·0458	1·0213	0·9879
16·79	1·1413	1·1332	1·1251	1·1170	1·1090	1·0929	1·0768	1·0518	1·0178
32·53	1·1730	1·1645	1·1559	1·1473	1·1388	1·1221	1·1054	1·0791	1·0428
42·39	1·1927	1·1839	1·1750	1·1662	1·1575	1·1403	1·1231	1·0953	1·0575
48·81	1·2047	1·1958	1·1869	1·1779	1·1690	1·1512	1·1334	1·1050	1·0665
50·31	1·2076	1·1987	1·1897	1·1807	1·1717	1·1539	1·1361	1·1073	1·0682
53·28	1·2130	1·2040	1·1950	1·1860	1·1770	1·1590	1·1408	1·1119	1·0722
54·94	1·2158	1·2068	1·1977	1·1885	1·1794	1·1613	1·1434	1·1140	1·0742
57·92	1·2205	1·2114	1·2023	1·1932	1·1840	1·1657	1·1474	1·1176	1·0773
63·42	1·2284	1·2190	1·2097	1·2003	1·1908	1·1720	1·1533	1·1233	1·0823
72·18	1·2405	1·2306	1·2207	1·2108	1·2008	1·1813	1·1617	1·1312	1·0894
86·66	1·2585	1·2476	1·2365	1·2255	1·2151	1·1943	1·1734	1·1414	1·0977
100·00	1·2741	1·2626	1·2512	1·2399	1·2284	1·2060	1·1834	1·1490	1·1028

FIG. 6.

o-Chlorophenol and diphenylmethylamine.

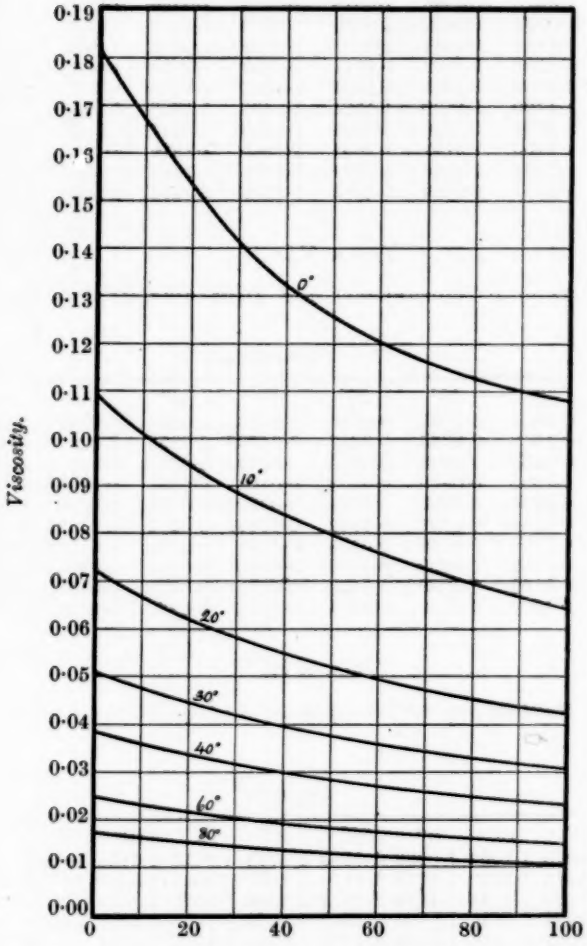


Table VII*a*.

Mixtures of o-Chlorophenol and Quinoline.

Weight per cent. of *o*-chloro-phenol.	Viscosities.								
	0°	10°	20°	30°	40°	60°	80°	110°	150°
0·00	0·0683	0·0480	0·0364	0·0294	0·02385	0·01671	0·01250	0·00930	0·00666
16·79	0·1450	0·0950	0·0662	0·0487	0·0371	0·02380	0·01673	0·01129	0·00745
32·53	0·415	0·2221	0·1300	0·0911	0·0635	0·03595	0·02222	0·01334	0·00815
42·39	1·125	0·503	0·2362	0·1440	0·0896	0·0440	0·02595	0·01462	0·00857
48·81	2·250	0·770	0·3345	0·1792	0·1047	0·0484	0·02760	0·01505	0·00869
50·31	2·555	0·825	0·3510	0·1840	0·1073	0·0490	0·02775	0·01505	0·00868
53·28	2·935	0·902	0·3690	0·1900	0·1095	0·0494	0·02785	0·01502	0·00865
54·94	3·017	0·926	0·3725	0·1901	0·1098	0·0493	0·02775	0·01494	0·00860
57·92	3·014	0·923	0·3662	0·1888	0·1089	0·0488	0·02700	0·01469	0·00850
63·42	2·450	0·804	0·3162	0·1742	0·1000	0·04525	0·02560	0·01411	0·00822
72·18	1·341	0·4815	0·2185	0·1282	0·0764	0·03695	0·02205	0·01266	0·00759
86·66	0·3935	0·1818	0·0995	0·0641	0·0433	0·02425	0·01600	0·01007	0·00650
100·00	0·1079	0·0639	0·0421	0·0308	0·0232	0·01513	0·01070	0·00760	0·00546

Table VII*b*.

Mixtures of o-Chlorophenol and Quinoline.

Weight per cent. of *o*-chloro-phenol.....	57·0	56·25	55·5	55·0	54·5	53·5	52·5	51·5	51·0
Temperature ...	0°	10°	20°	30°	40°	60°	80°	110°	150°

Table VIII.

Mixtures of o-Chlorophenol and Pyridine.

Weight per cent. of *o*-chloro-phenol.	Densities.							
	0°	10°	20°	30°	40°	60°	80°	110°
0·00	1·0013	0·9916	0·9819	0·9723	0·9627	0·9424	0·9218	0·8900
11·17	1·0288	1·0190	1·0093	0·9995	0·9896	0·9696	0·9498	0·9198
21·62	1·0555	1·0459	1·0364	1·0267	1·0171	0·9976	0·9783	0·9492
31·57	1·0821	1·0726	1·0631	1·0536	1·0441	1·0250	1·0058	0·9770
42·31	1·1123	1·1030	1·0937	1·0843	1·0750	1·0561	1·0373	1·0080
51·48	1·1402	1·1308	1·1213	1·1120	1·1027	1·0839	1·0651	1·0357
60·15	1·1674	1·1580	1·1486	1·1392	1·1297	1·1110	1·0921	1·0622
67·47	1·1894	1·1798	1·1701	1·1605	1·1509	1·1318	1·1124	1·0822
72·50	1·2040	1·1941	1·1843	1·1743	1·1645	1·1447	1·1247	1·0942
76·93	1·2162	1·2062	1·1963	1·1860	1·1759	1·1559	1·1358	1·1048
81·06	1·2272	1·2171	1·2066	1·1961	1·1857	1·1654	1·1450	1·1139
85·17	1·2384	1·2278	1·2177	1·2064	1·1958	1·1753	1·1548	1·1232
92·51	1·2562	1·2453	1·2344	1·2236	1·2128	1·1915	1·1703	1·1376
100·00	1·2741	1·2626	1·2512	1·2399	1·2284	1·2060	1·1834	1·1490

FIG. 7.

o-Chlorophenol and quinoline.

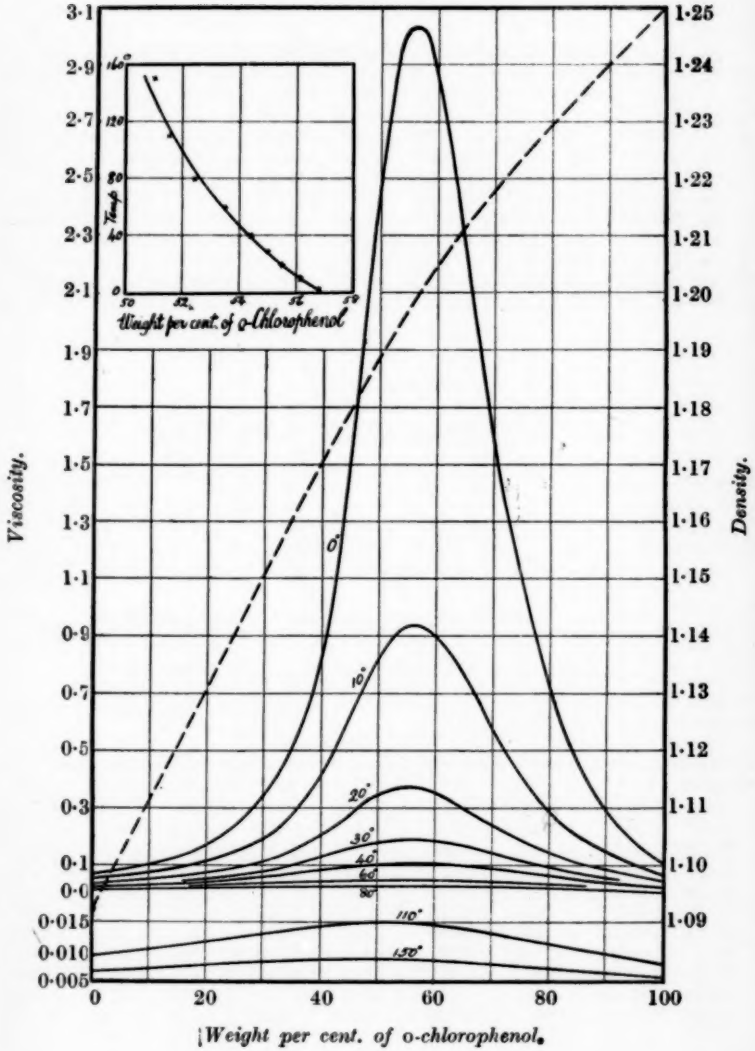


TABLE VIII*a*.

Mixtures of o-Chlorophenol and Pyridine.

Weight per cent. of *o*-chloro-phenol.	Viscosities.							
	0°	10°	20°	30°	40°	60°	80°	110°
0·00	0·01323	0·01108	0·00941	0·00821	0·00714	0·00578	0·00487	0·00385
11·17	0·01661	0·01382	0·01158	0·00994	0·00863	0·00686	0·00568	0·00448
21·62	0·02175	0·01765	0·01459	0·01249	0·01073	0·00830	0·00672	0·00516
31·57	0·02985	0·0235	0·01903	0·01588	0·01351	0·01015	0·00802	0·00600
42·31	0·0445	0·0336	0·02620	0·02152	0·01773	0·01291	0·00986	0·00704
51·48	0·0710	0·0508	0·0369	0·02960	0·02310	0·01592	0·01185	0·00798
60·15	0·1198	0·0777	0·0528	0·0392	0·02980	0·01935	0·01370	0·00885
67·47	0·1828	0·1076	0·0682	0·0472	0·0353	0·02181	0·01487	0·00945
72·51	0·2285	0·1275	0·0780	0·0522	0·0378	0·02285	0·01529	0·00964
76·93	0·2630	0·1385	0·0823	0·0540	0·0384	0·02290	0·01532	0·00962
81·06	0·2695	0·1402	0·0816	0·0536	0·0378	0·02230	0·01495	0·00942
85·17	0·2506	0·1326	0·0758	0·0504	0·0355	0·02108	0·01425	0·00906
92·51	0·1810	0·1004	0·0597	0·0411	0·0294	0·01840	0·01257	0·00837
100·00	0·1079	0·0639	0·0421	0·0308	0·02320	0·01513	0·01070	0·00760

TABLE VIII*b*.

Mixtures of o-Chlorophenol and Pyridine.

Weight per cent. of Chlorophenol ...	80·0	78·75	78·0	76·5	75·0	73·5	72·0	70·5
Temperature ...	0°	10°	20°	30°	40°	60°	80°	110°

o-Chlorophenol, like many other phenolic substances, forms a compound with acetone, about which more details will be given in Part III. On account of the absence of any indication of a compound in the viscosity–composition curves for mixtures of phenol and acetone, it was thought advisable to study mixtures of *o*-chlorophenol and acetone in order to ascertain whether, having eliminated the disturbing influence of molecular association of the phenol, the viscosity–composition curve was still of the sagged type or showed any indication of the formation of a compound. The results of these measurements are given in tables IX, IX*a*, and IX*b*. During the course of these experiments it was found possible to heat a mixture of *o*-chlorophenol and acetone containing not less than about 60 per cent. of the former to 70° for some time without appreciable loss of acetone; the measurements recorded in table IX*b* could, therefore, be made with certainty as regards the mixtures retaining their original composition. Fig. 9 shows graphically the results of the viscosity measurements. The density curves for these mixtures are very slightly sagged.

FIG. 8.

o-Chlorophenol and pyridine.

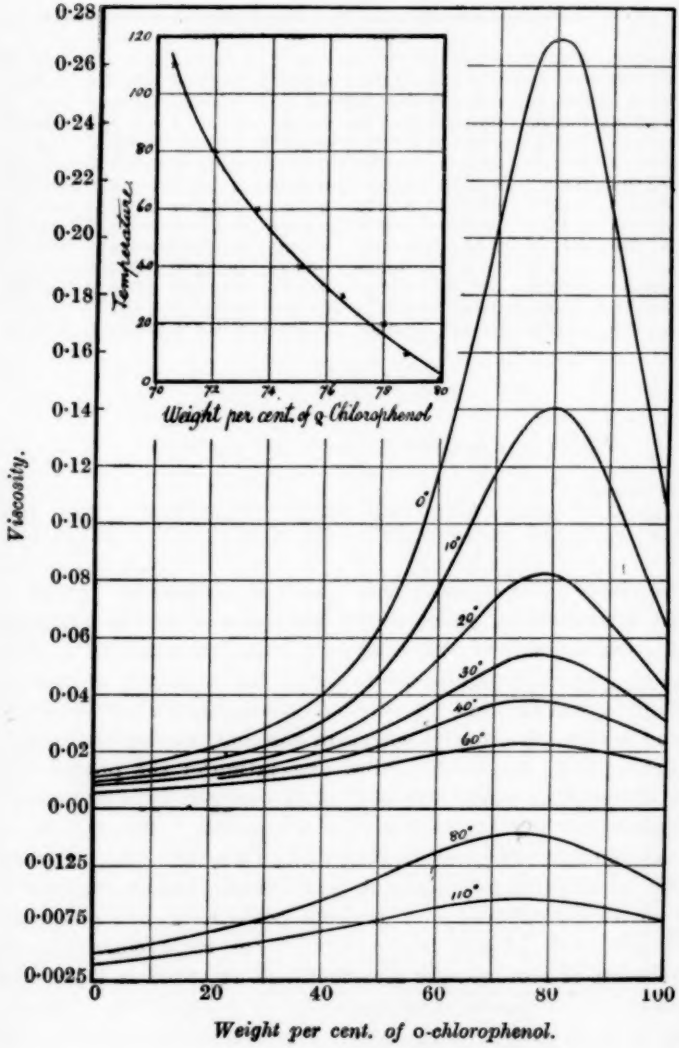


TABLE IX.

Mixtures of o-Chlorophenol and Acetone.

Weight per cent. of *o*-chloro-phenol.	Densities.					
	0°	10°	20°	30°	40°	50°
0·00	0·8146	0·8030	0·7912	0·7793	0·7674	0·7555
18·49	0·8799	0·8688	0·8576	0·8464	0·8352	0·8240
32·38	0·9363	0·9255	0·9147	0·9039	0·8930	0·8821
49·95	1·0138	1·0032	0·9924	0·9818	0·9712	0·9604
60·49	1·0639	1·0533	1·0427	1·0321	1·0215	1·0109
71·01	1·1176	1·1069	1·0962	1·0856	1·0748	1·0642
83·22	1·1826	1·1718	1·1609	1·1501	1·1393	1·1285
91·73	1·2284	1·2172	1·2060	1·1948	1·1836	1·1725
100·00	1·2741	1·2626	1·2512	1·2399	1·2284	1·2172

TABLE IX*a*.

Mixtures of o-Chlorophenol and Acetone.

Weight per cent. of *o*-chloro-phenol.	Viscosities.					
	0°	10°	20°	30°	40°	50°
0·00	0·003955	0·00360	0·003235	0·00295	0·00270	0·00248
18·49	0·00582	0·00527	0·00475	0·00419	0·00382	0·003515
32·38	0·00787	0·00692	0·00611	0·00569	0·00508	0·00465
49·95	0·01398	0·01162	0·00992	0·00893	0·00777	0·00687
60·49	0·02135	0·01682	0·01376	0·01199	0·01019	0·00893
71·01	0·0359	0·02675	0·02051	0·01684	0·01369	0·01154
83·22	0·0675	0·0447	0·0317	0·0240	0·01886	0·01527
91·73	0·0940	0·0580	0·0391	0·0285	0·02165	0·01735
100·00	0·1079	0·0639	0·0421	0·0308	0·0232	0·01871

TABLE IX*b*.

Mixtures of o-Chlorophenol and Acetone.

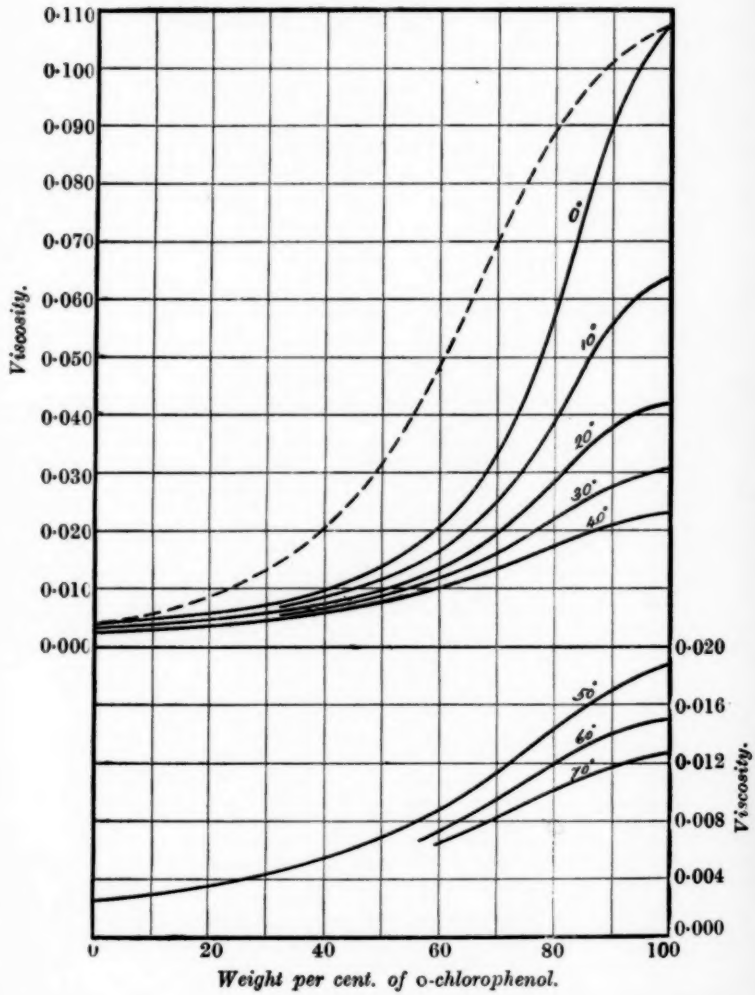
Weight per cent. of *o*-chloro-phenol.	Densities.		Viscosities.	
	60°	70°	60°	70°
59·37	0·9948	0·9837	0·00729	0·00641
68·23	1·0391	1·0280	0·00918	0·00791
76·99	1·0848	1·0736	1·01107	0·00952
84·64	1·1242	1·1130	0·01289	0·01087
91·08	1·1581	1·1468	0·01422	0·01187
100·00	1·2060	1·1947	0·01513	0·01266

Hewitt and Winmill made measurements of the surface tension of *o*-nitrophenol, and deduced the value 0·84 for the association factor for this substance in the liquid state. Now any number less than unity for the association factor of a liquid substance is unintelligible, and such a figure is an indication either of some experimental error or of the inapplicability of the method used. Never-

theless, this low figure may be taken as an indication that there is little, if any, association of the molecules of pure liquid *o*-nitrophenol.

FIG. 9.

o-Chlorophenol and acetone.



The dissociation constants of phenol, *o*-chlorophenol, and *o*-nitrophenol given in Landolt's tables are as follows:

Phenol	1·09 to 1·30 $\times 10^{-10}$ at 25°
o-Chlorophenol	7·7 $\times 10^{-10}$ at 25°
o-Nitrophenol.....	6·8 $\times 10^{-8}$ at 25°

from which it appears that *o*-nitrophenol is about one hundred times stronger an acid than *o*-chlorophenol, and six hundred times stronger than phenol; hence, it would seem as if *o*-nitrophenol possessed to a still higher degree the advantages claimed for *o*-chlorophenol for the purposes of this investigation. It has, however, the disadvantage of having a rather high melting point, and, moreover, it is a substance which is very difficult to undercool without crystallisation taking place.

Mixtures of *o*-nitrophenol with aniline, quinoline, and pyridine were examined at four temperatures, namely, 30°, 40°, 60°, and 80°, and the results obtained are given in tables X, XI, and XII. The viscosities are represented graphically in the corresponding figures.

Table X.

Mixtures of o-Nitrophenol and Aniline.

Weight per cent. of *o*-nitrophenol.	Densities.				Viscosities.			
	30°	40°	60°	80°	30°	40°	60°	80°
0·00	1·0131	1·0045	0·9872	0·9700	0·03145	0·02405	0·01543	0·01100
10·88	1·0376	1·0288	1·0109	0·9933	0·02972	0·02322	0·01512	0·01094
22·36	1·0655	1·0566	1·0382	1·0202	0·02863	0·02257	0·01486	0·01086
32·77	1·0924	1·0833	1·0645	1·0460	0·02805	0·02224	0·01477	0·01081
42·00	1·1175	1·1080	1·1888	1·0699	0·02802	0·02215	0·01478	0·01088
51·28	1·1445	1·1350	1·1150	1·0955	0·02828	0·02230	0·01494	0·01100
60·52	1·1717	1·1620	1·1419	1·1222	0·02881	0·02272	0·01525	0·01127
68·32	1·1968	1·1867	1·1663	1·1462	0·02952	0·02328	0·01564	0·01155
77·11	1·2263	1·2162	1·1954	1·1748	0·03068	0·02415	0·01622	0·01199
85·04	1·2531	1·2428	1·2216	1·2008	0·03225	0·02515	0·01688	0·01248
91·49	(1·2745)	1·2642	1·2429	1·2218	(0·0339)	0·02610	0·01741	0·01289
100·00	(1·3045)	1·2942	1·2712	1·2482	(0·0365)	0·02755	0·01825	0·01348

Table XI.

Mixtures of o-Nitrophenol and Quinoline.

Weight per cent. of *o*-nitrophenol.	Densities.				Viscosities.			
	30°	40°	60°	80°	30°	40°	60°	80°
0·00	1·0850	1·0773	1·0615	1·0458	0·0294	0·02385	0·01671	0·01250
10·80	1·1072	1·0989	1·0823	1·0657	0·03361	0·02660	0·01789	0·01321
21·43	1·1312	1·1224	1·1050	1·0879	0·03772	0·02928	0·01897	0·01391
30·69	1·1520	1·1430	1·1249	1·1069	0·04125	0·03160	0·01995	0·01437
41·61	1·1760	1·1667	1·1479	1·1291	0·04495	0·03375	0·02084	0·01470
49·16	1·1940	1·1844	1·1651	1·1458	0·0468	0·03465	0·02122	0·01483
58·20	1·2142	1·2045	1·1846	1·1649	0·0472	0·03470	0·02122	0·01485
67·04	1·2341	1·2242	1·2038	1·1836	0·04595	0·03410	0·02093	0·01471
77·56	1·2553	1·2456	1·2246	1·2038	0·04355	0·03250	0·02024	0·01441
82·41	1·2659	1·2561	1·2348	1·2138	0·0422	0·03151	0·01986	0·01421
86·76	1·2750	1·2651	1·2435	1·2220	0·0409	0·03059	0·01949	0·01406
91·18	1·2846	1·2746	1·2525	1·2306	0·0395	0·02955	0·01909	0·01392
95·54	(1·2943)	1·2842	1·2617	1·2393	(0·0380)	0·02855	0·01874	0·01371
100·00	(1·3045)	1·2942	1·2712	1·2482	(0·0365)	0·02755	0·01825	0·01348

FIG. 10.

o-Nitrophenol and aniline.

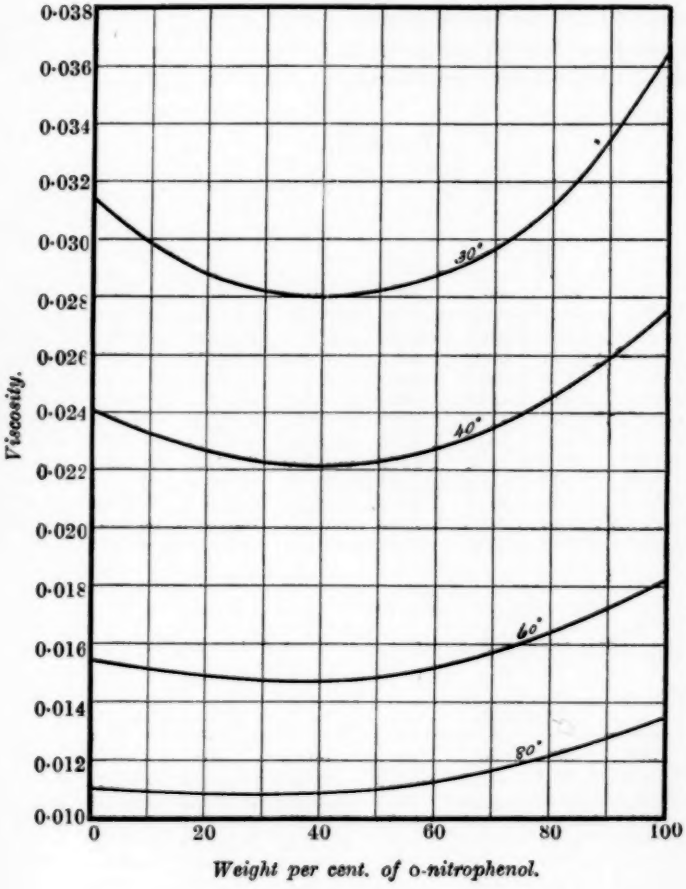


TABLE XII.

Mixtures of o-Nitrophenol and Pyridine.

Weight per cent. of *o*-nitrophenol.	Densities.				Viscosities.			
	30°	40°	60·1°	80°	30°	40°	60·1°	80°
0·00	0·9723	0·9627	0·9424	0·9218	0·00821	0·00714	0·00578	0·00487
11·32	1·0047	0·9947	0·9740	0·9536	0·00943	0·00815	0·00647	0·00539
20·74	1·0331	1·0231	1·0022	0·9816	0·01081	0·00930	0·00719	0·00590
27·58	1·0544	1·0442	1·0232	1·0025	0·01211	0·01030	0·00786	0·00635
39·62	1·0935	1·0831	1·0617	1·0407	0·01500	0·01245	0·00925	0·00724
52·25	1·1362	1·1257	1·1037	1·0824	0·01881	0·01510	0·01092	0·00836
60·24	1·1645	1·1537	1·1317	1·1103	0·02150	0·01711	0·01212	0·00911
68·32	1·1929	1·1821	1·1599	1·1383	0·02450	0·01912	0·01325	0·00992
76·79	1·2233	1·2125	1·1903	1·1686	0·02755	0·02145	0·01460	0·01080
86·96	1·2578	1·2472	1·2250	1·2035	0·03145	0·02411	0·01621	0·01195
91·25	(1·2730)	1·2622	1·2400	1·2185	0·03331	0·02525	0·01688	0·01240
100·00	(1·3045)	1·2942	1·2712	1·2482	(0·0365)	0·02755	0·01825	0·01348

Discussion of Results.

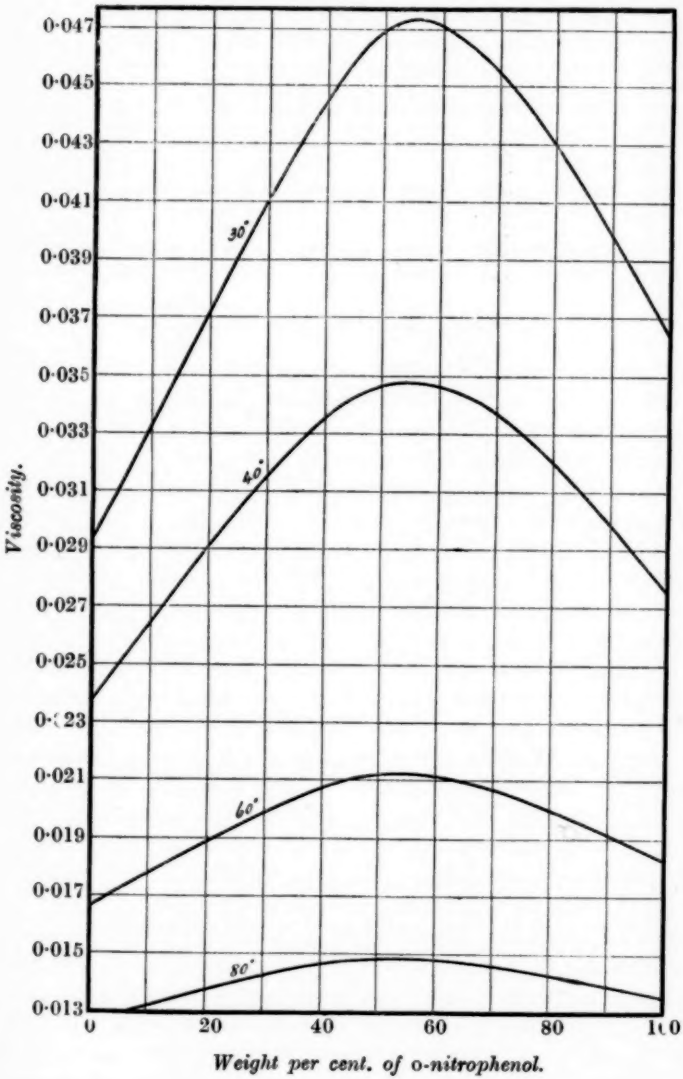
In the discussion of the viscosities of mixtures containing phenol given in Part I. (*loc. cit.*) it was pointed out that where the formation of compounds took place the viscosity of the mixture was, in general, greater than the calculated mean; there was also an indication in the results obtained with the phenol mixtures that the stronger the base the greater was this difference. The results obtained with mixtures containing *o*-chlorophenol show clearly that the substitution of this more strongly acidic compound for phenol influenced the character of the viscosity–composition curves in a manner that was to be expected, namely, more pronounced and sharper maxima in the case of mixtures containing aniline and quinoline, and very marked maxima on the viscosity–composition curves for mixtures containing dimethylaniline and pyridine. One fact, however, remains the same; neither the maximum point nor the position of maximum deviation on the viscosity–composition curve remains constant with rise in temperature, although the shift of the latter, as indicated by the small curves inset in the figures, is decidedly less than is the case with the mixtures containing phenol.

Although it is very doubtful whether the disturbing factor of molecular association has been eliminated in the case of the *o*-chlorophenol mixtures, it is undoubtedly very much less than in the case of the phenol mixtures. It is, moreover, significant that the position of maximum deviation from the calculated value of the viscosity, especially in those mixtures containing aniline and quinoline, lies much nearer the position corresponding with equimolecular proportions in the *o*-chlorophenol mixtures than in the corresponding mixtures containing phenol. The fact remains, however, that

in all cases, especially where dimethylaniline or pyridine is one of the components, and the more so the lower the temperature, the

FIG. 11.

o-Nitrophenol and quinoline

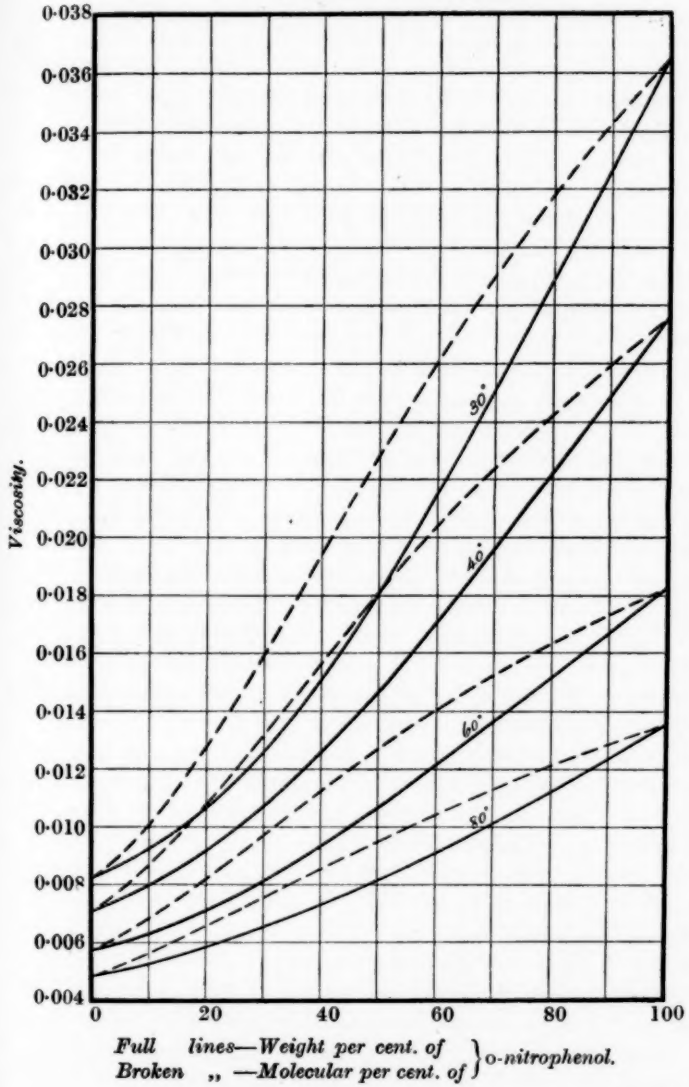


point on the viscosity–composition curve which lies farthest away from the straight line representing the calculated means does not

coincide with that required for equimolecular or any other simple molecular proportion. For mixtures of *o*-chlorophenol with aniline

FIG. 12.

o-Nitrophenol and pyridine.



or quinoline it lies within 1 or 2 per cent. of the equimolecular value for a temperature of 80°, whilst for mixtures of *o*-chloro-

phenol with pyridine there is a difference of about 10 per cent., and with dimethylaniline a difference of 23 per cent. for the same temperature. There is, apparently, some other factor that has not been taken into consideration.

Any attempt to explain all the differences and peculiarities of the viscosity–composition curves described in the foregoing pages and in other work on this subject generally, must of necessity involve some theory as to the nature and cause of liquid friction. The suggestion put forward by Jones and Veazey (*Amer. Chem. J.*, 1907, **37**, 405) that the degradation of associated into simple molecules results in an increase in the viscosity because of the greater area of frictional surfaces which come into contact with one another, may be dismissed at once for the two following reasons:

(1) There is no justification for the assumption that the larger number of molecular surface contacts resulting from the splitting up of large into smaller molecules will result in a higher viscosity. If this were so, substances with small molecules should have higher viscosities than similar substances of higher molecular weight; the viscosities of the members of any homologous series of compounds should decrease as the series is ascended. Dunstan and his collaborators have shown that the viscosities of the members of any homologous series, except the first member or two in one or two cases, increase with rise in molecular weight.

(2) There is every reason to suppose that any action which brings about the dissociation of the associated molecules of a substance, unless it is accompanied by some counterbalancing effect, will produce a lowering of the viscosity. The large number of sagged viscosity curves for mixtures of liquids which are chemically indifferent towards each other is evidence of this.

From theoretical considerations, Bousfield has deduced a relationship between the viscosity of a liquid and the size of the molecules, according to which the viscosity is a simple function of the radions of the substances present in the liquid (*Phil. Trans.*, [*A*], 1906, **206**, 134, and T., 1915, **107**, 1781). This is in direct opposition to Jones and Veazey's theory, but cannot itself be regarded as satisfactory. A complete theory of the viscosity of liquids must involve much more than the mere size of the molecules.

All liquids possess to a greater or less extent the property of cohesion, and this may be the chief cause of the resistance to motion in a liquid. In the case of a liquid which contains associated molecules, or of a liquid mixture of two substances in which there is a partial combination of the two components, the molecular complexes, whether they consist of associated molecules of a pure

substance or of a combination of the two components in the case of a binary mixture, are, in all probability, not independent molecular aggregates which move about indifferently in the mass of the liquid, but members of a complex system in which there is a continuous interchange of the smaller units: the equilibrium is not a statical, but a dynamical one. Any factor that facilitates the interchange of the units in such a system will tend to lower the viscosity, and conversely, any factor that makes such an interchange more difficult will tend to raise the viscosity. It will be shown subsequently that the dielectric constant of the liquid is, in all probability, an important factor in this connexion.

From the foregoing considerations it will be evident that the viscosity of a mixture of two substances, neither of which contains associated molecules, but which unite together to some extent, forming a compound, should be greater than the calculated mean, and the maximum difference should occur at the point where the mixture contains the maximum proportion of the compound formed. The results obtained with the various mixtures examined will now be considered in detail.

All the mixtures containing phenol or cresol may be said to have abnormal viscosity curves because of the disturbing effect of the associated molecules of phenol or cresol. Other factors, such as the existence of more than one compound, as in mixtures of phenol and pyridine, *p*-cresol and pyridine, and phenol and quinoline, in which, as will be shown in Part III., two compounds are produced, may also be contributory causes of abnormality.

All the substances mixed with *o*-chlorophenol, except diphenylmethylamine, form compounds the compositions of which correspond with equimolecular proportions of the two components (see Part III.). In the mixtures of *o*-chlorophenol with aniline and quinoline the position of maximum deviation of the viscosity curve from the linear is not far removed from that corresponding with equimolecular proportions. Such differences as these may be caused by association to a small extent of the *o*-chlorophenol molecules. It should be mentioned here that no account has been taken of the possible association of the molecules of the basic component, and abnormalities in the viscosity curves that have been attributed to the association of the phenolic component of the mixture should more probably be ascribed to the difference in the degree of association of the two component substances.

Mixtures of *o*-chlorophenol and dimethylaniline show a maximum deviation of viscosity far removed from the position of equimolecular proportions. It should be noted, however, that the composition of the mixture of these two substances which contains the maxi-

mum proportion of compound does not correspond with the equimolecular value, but contains about 10 per cent. more *o*-chlorophenol (see Part IV.); hence the difference between the composition of this mixture and that the viscosity of which shows the greatest deviation from the calculated mean amounts to about 13 per cent. at 80°.

It is claimed by Dunstan and Thole (*J. Chim. phys.*, 1909, **7**, 204) that the values of the expression $\frac{\eta \times 10^6}{\text{mol. vol.}^3}$, where η represents the viscosity, give some indication as to the degree of molecular complexity of a substance in the liquid state. Mussell, Thole, and Dunstan (T., 1912, **101**, 1008) and Thole (T., 1913, **103**, 317) determined the values of this expression for aniline and several of its derivatives with the following results:

	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$		
	25°	55°	130°
Aniline	398	182	55·5
Methylaniline	185	96·9	—
Dimethylaniline	101	64·7	—

The value of the expression $\frac{\eta \times 10^6}{\text{mol. vol.}}$ for a large number of unassociated substances lies between 40 and 70. Although it is very doubtful whether much importance can be attached to any quantitative significance of the above figures, they may be taken as an indication, in a qualitative way, that the substitution of methyl groups for the amino-hydrogen in aniline has a distinct lowering effect on the association of the molecules. Similar results were obtained with the ethylanilines, and it was also shown that diphenylmethylamine gives a considerably lower value than does diphenylamine. The lowering of the viscosity with increasing molecular weight of such closely related substances certainly indicates that the introduction of the alkyl groups has had some simplifying effect on the molecules of these substances in the liquid state.

It seems fairly evident that there is a certain amount of molecular complexity in these basic compounds, and that it is greater in aniline than it is in dimethylaniline. The greater difference, in the case of the mixtures of *o*-chlorophenol and dimethylaniline, between the composition of the mixture which shows the maximum deviation in viscosity from the calculated mean and that which contains the largest proportion of compound may thus be explained.

In a similar manner, the difference between the position of maxi-

mum deviation on the viscosity curve for mixtures of *o*-chlorophenol and pyridine and that required by equimolecular proportions of the two components may be explained. In many respects the viscosity curves for mixtures of *o*-chlorophenol with dimethylaniline and pyridine are similar, but there are one or two points of difference which are worthy of consideration. The maxima on the curves for the latter of these two mixtures are sharper and higher than in the dimethylaniline mixtures. Pyridine is a much stronger base than dimethylaniline, and its salt-forming properties are correspondingly greater; consequently there will be more extensive compound formation in the mixtures containing pyridine than in corresponding mixtures containing dimethylaniline, and this will account for the difference just mentioned. Another difference between these two sets of curves lies in their slope between the ends corresponding with the pure bases and the maximum positions. With the mixtures containing pyridine, the sag of the curves between these two points is much greater than is the case with the corresponding dimethylaniline mixtures. Now pyridine is well known as a good ionising solvent; its dielectric constant is fairly high. Such solvents, in general, do not promote association; solutions of hydroxylic compounds in them give molecular weights which are approximately normal, whereas these substances, when dissolved in solvents of low dielectric constant, show evidence of considerable molecular association.

This absence of molecular association may be the manifest result of the greater facility with which the interchange of the molecular units is brought about by the high dielectric constant of the medium; and the same force which prevents molecular association might even oppose the formation of compounds; for if the formation of compounds such as are now under consideration, and the complex, associated molecules of a pure substance may be but a particular type, results from a force electrical in origin, then a molecule of the compound may be likened to a small condenser the conductors of which are the two component parts of the compound molecule. The force of attraction between the two conductors will be inversely proportional to the specific inductive capacity of the dielectric; hence, in order to interpose a certain distance between the two parts of the molecule, work will have to be done the magnitude of which will be inversely proportional to the dielectric constant of the medium. Thus it follows that the interchange of the molecular units in a system in which compound or complex molecules are in dynamic equilibrium with simpler ones is facilitated by a high dielectric constant, and the liquid will, on that account, offer less resistance to motion and have a low viscosity.

In view of the foregoing considerations, some explanation of the peculiar character of the viscosity curves for the mixtures containing acetone may now be attempted. Acetone and *o*-chlorophenol form a compound which contains equimolecular proportions of the two constituents (see Part III.). The shape of the middle portion of the freezing-point curve indicates that at $-40°$ there is an appreciable amount of dissociation. There is, however, certain evidence (see Part IV.) that a considerable amount of the compound exists in the mixture at temperatures above 0°. The viscosity curves for this mixture have no maxima, but, unlike the corresponding curves for mixtures of phenol and acetone, they all contain a point of inflection, and, what is also of some importance, the position of this point of inflection moves, with rise in temperature, from right to left of the diagram, that is, towards that end of the curves where the mixtures are rich in acetone. The drift of this point is slight, it is true, but definite. There is little evidence, in any form, of molecular association to any appreciable extent in acetone; the test by means of the formula suggested by Dunstan and Thole (*loc. cit.*), which usually gives values for the association factor enormously higher than those given by any other method, suggests no association. Moreover, the dielectric constant of acetone is about double that of pyridine, so that here we have what appears to be an extreme case for a mixture in which the formation of compounds takes place. The molecules of acetone are smaller than those of any other substance used in this investigation; the molecules of the compound acetone–*o*-chlorophenol are smaller than those of any of the other compounds, and their size may possibly be even smaller than the average size of the molecules of *o*-chlorophenol itself, and consequently, the average size of the molecules, or Bousfield's radion, may increase continuously throughout the whole range of mixtures from pure acetone to pure *o*-chlorophenol. This is even more probable in the acetone–phenol mixtures. These factors, together with the effect of the high dielectric constant of acetone, all tend to produce a low viscosity of the mixtures, especially those containing an appreciable amount of acetone. It will be now evident that the difference between the viscosity curves for the acetone–phenol mixtures and those for mixtures of acetone and *o*-chlorophenol, namely, the presence of a point of inflection on the latter set of curves and its absence on the former, may be accounted for by the greater association of the phenol molecules.

It will be convenient at this stage, before proceeding to discuss the *o*-nitrophenol mixtures, to consider the influence of rise in temperature on the various factors already dealt with.

(1) The temperature-coefficient of molecular association is always negative.

(2) The dissociation constant generally increases with rise in temperature; hence, the combining power may be assumed to be augmented by raising the temperature.

(3) The dielectric constant is diminished by rise in temperature.

(4) Rise in temperature promotes thermal dissociation of such compounds as are here dealt with.

The effect of raising the temperature, therefore, so far as factors (1), (2), and (3) are concerned, will be to increase the relative amount of compound formed, and thus accentuate its influence on the physical properties of the mixture. Factor (4) will have the opposite effect. It is evident from the fact that all the small curves inset in the various figures are of one type, with rise in temperature they all approach the position corresponding with equimolecular proportions of the components, or of maximum compound formation, the effects of factors (1), (2), and (3) more than counterbalance the effect of factor (4). Further, it appears possible that as a result of the combined effects of factors (2), (3), and (4) a rise in temperature might be accompanied by an actual increase in the amount of compound formed. It will be shown in Part IV. that this is probably the case in at least one of the mixtures studied.

As regards the mixtures of *o*-chlorophenol and diphenylmethylamine little can be said excepting that, if any compound between these two substances is formed, its presence, so far as the viscosity curves indicate, is entirely masked by association of one or both of the components.

The results obtained in the case of mixtures of *o*-nitrophenol with aniline, quinoline, and pyridine are very puzzling. The value of the dissociation constant for *o*-nitrophenol ($6{\cdot}8 \times 10^{-8}$ at 25°) is nearly a hundred times that of *o*-chlorophenol ($7{\cdot}7 \times 10^{-10}$ at 25°), yet there is certainly far less compound formed in the mixtures containing the former of these two substances than in the corresponding mixtures containing *o*-chlorophenol. Evidence to this effect has already been obtained by Philip (T., 1903, **83**, 814). When liquid *o*-nitrophenol is mixed with quinoline there is a very slight deepening in colour, which, since the salts of *o*-nitrophenol and their solutions are more highly coloured than *o*-nitrophenol itself, may be taken as an indication that the formation of compounds does take place to some extent. No such deepening in colour, however, is apparent when *o*-nitrophenol is mixed with aniline or with pyridine. That there is some slight combination with the latter of these two substances is evident from the fact

that a liquid mixture of *o*-nitrophenol and pyridine is a fairly good conductor of electricity, whereas both these two substances in the pure state are virtually non-conductors.

The introduction of a nitro-group into a compound generally results in a large increase in the dielectric constant, and this, for the reason already given, may be one cause of the small amount of compound formed. Steric hindrance caused by the nitro-group also plays an important part in preventing the formation of compounds in these mixtures.

So far as viscosity measurements go, of the three mixtures examined which contain *o*-nitrophenol, only the one containing quinoline can be said to give any definite indication of the formation of compounds.

The question has been raised as to whether viscosity should be plotted against molecular composition of the mixture instead of against weight per cent.; some investigators prefer one method and some the other. The two methods will give slightly different results except when the molecular weights of the two components are equal, and the difference will be the greater the more the molecular weights of the two substances differ. The broken-line curves in Figs. 9 and 12 show the viscosities plotted against molecular per cent. These are the extreme cases; in all the others the difference in the results obtained and those derivable from this other method of plotting would be inappreciable. As to which is the correct method depends, of course, on whether viscosity is a molecular property or a property of mass. Until other factors which influence viscosity can be eliminated, or correctly allowed for, it will be impossible to decide this point.

As a result of this investigation, the following general conclusions may be drawn:

(1) Any change which tends to simplify the molecular state of a liquid will produce a lowering of the viscosity, and conversely, any change which tends to increase the complexity of the molecular state of a liquid will cause an increase in viscosity.

(2) The viscosity–composition curve for a mixture of two indifferent substances should be a straight line; the sag of the curves which is generally present in such cases may be attributed to the dissociating effect of the two components on one another.

(3) A liquid mixture of two substances which react chemically with one another forming an additive compound should have a higher viscosity than the calculated mean, the maximum difference occurring with that mixture which contains the largest proportion of the compound. Such deviations as are frequently encountered

may be traced to the disturbing influence of molecular association of the components and their unequal dissociating powers.

(4) As an independent physical test of compound-formation in liquid mixtures, and especially as a means of determining the composition of such compounds, the property of viscosity, influenced as it is by so many factors, is untrustworthy.

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XXXVII.—*The Study of Binary Mixtures. Part III. Freezing-point Curves.*

By ARTHUR BRAMLEY.

IN two previous communications (this vol., pp. 10 and 434) an account was given of the measurements of the viscosities of a number of binary mixtures, many of which were known to contain compounds formed by the union of the two components of the system. Our knowledge of the existence and composition of these compounds, and, to a certain extent, of their stability, is based on the work of Schreinemakers (*Zeitsch. physikal. Chem.*, 1899, **31**, 581); of Philip (T., 1903, **83**, 814); of Kremann (*Monatsh.*, 1906, **27**, 91); and of Schmidlin and Lang (*Ber.*, 1910, **43**, 2812), who determined the freezing-point curves of some of these mixtures.

As a result of the classical work on this subject carried out by Guthrie on mixtures of inorganic salts; by Heycock and Neville on mixtures of metals; and by Roozeboom on salt hydrates, and, during more recent times, by the investigators previously mentioned, together with a number of others on similar mixtures and mixtures of a large number of organic substances, we now know that the freezing-point curves of mixtures afford valuable and trustworthy information as to the presence and composition of compounds that may be formed by the union of the components of the system.

The freezing-point curves of a number of the mixtures the densities and viscosities of which have been described in Parts I. and II. (*loc. cit.*) have not previously been determined, and on account of the uncertainty that seems inseparable from any deduction, based on measurements of viscosity, as to the presence and composition of compounds in these mixtures, it seemed desirable to obtain more trustworthy information on this point. It was therefore decided

to determine the freezing-point curves of some of those mixtures which had not been previously examined in this respect, and the following is an account of the experiments made in this connexion.

Experimental.

Since many of the substances dealt with have fairly low melting points, it was obvious from the outset that temperatures would be encountered which could not be determined by means of a mercurial thermometer. A platinum resistance thermometer, which was made by the Cambridge Scientific Instrument Co., was therefore used. The bulb, that is the portion of the tube containing the resistance coil, was of about the same diameter as the bulb of an ordinary Beckmann thermometer and about 3·5 cm. long. The fundamental interval of the thermometer, that is, the difference in resistance of the thermometer between 0° and 100°, was 0·9965 ohm. The resistances were measured by means of a Callendar and Griffiths self-testing bridge and a very sensitive suspended-coil galvanometer, both of which instruments were supplied by the Cambridge Scientific Instrument Co.

The denominations of the resistance coils in the bridge were in hundredths of an ohm, and the bridge wire had a resistance of 0·01 ohm per cm., so that apart from the usual corrections that have to be applied, each cm. of the bridge wire represented a degree Centigrade. As regards the method of reduction of the temperatures from the platinum scale to the gas scale, there seems to be a considerable disagreement. In Callendar and Griffiths' difference formula:

$$t - pt = \Delta = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100}$$

in which Δ stands for the difference in temperature between t, the temperature on the air thermometer, and pt the temperature on the platinum scale, the value of the constant δ is generally very near to 1·5 for temperatures between 0° and 1000°. Below 0°, however, this value of δ ceases to give the proper correction. Moreover, it is well known that the presence of very slight impurities in the platinum has a considerable effect on its electrical resistance. On account of the uncertainty attending the use of the above formula for low temperatures, it was decided to make a comparison of the platinum-resistance thermometer used in these experiments with a constant-volume hydrogen-gas thermometer at two or three temperatures.

The fundamental interval of both thermometers was determined by means of melting ice and steam at atmospheric pressure. A mixture of solid carbon dioxide and ether was prepared by thor-

oughly stirring the two substances together until the mixture had the consistency of a thin paste, care being taken to break up all the lumps of solid carbon dioxide. This mixture was placed in a "Thermos" flask, and the bulbs of the two thermometers immersed in it, side by side. By stirring the mixture at intervals, the temperature was kept steady for several hours, and was, according to the gas thermometer, $-78{\cdot}35°$, and according to the platinum resistance thermometer $-81{\cdot}75°$; hence $\Delta = 3{\cdot}40$ for this temperature. This gives a value of $\delta = 2{\cdot}44$. A similar comparison of the two thermometers was made at the temperature of liquid air. The bulbs of the two thermometers were placed side by side in a silvered Dewar flask of about 1 litre capacity and nearly full of liquid air. The mean of three determinations with liquid air made at different times gave a temperature of $-188{\cdot}8°$ on the hydrogen thermometer and $-202{\cdot}1°$ on the platinum-resistance thermometer; the extreme variation in the three determinations was $0{\cdot}7°$. At $-190°$ the value of Δ was $13{\cdot}3$, which gives $\delta = 2{\cdot}42$.

Callendar (*Phil. Mag.*, 1899, [v], **47**, 191) has critically discussed this method of reduction, and on page 213 he gives some particulars of a platinum-resistance thermometer used by Dewar and Fleming, which, as regards variation in resistance, appears to be very similar to the one used in the experiments now being described. On the following page Callendar gives a table of reduction for Dewar and Fleming's thermometer, and this table has been used to reduce all the platinum temperatures obtained in these experiments to corresponding temperatures on the gas scale.

The mixtures were made up in a tube of the kind generally used in Beckmann's freezing-point apparatus. This was surrounded by a larger tube, which served as an air-jacket, and was supported in a wide, cylindrical Dewar tube containing the freezing mixture. The quantities of the substances used in the different mixtures are given in the various tables, from which it will be seen that generally 35—60 grams of mixture were employed. Cooling was produced by means of ice and salt whenever this mixture sufficed, but for the lower temperatures ether, cooled by means of liquid air, was used. An alcohol thermometer was used to determine the temperature of the cooling bath, which was easily adjusted to that required by adding liquid air or ether.

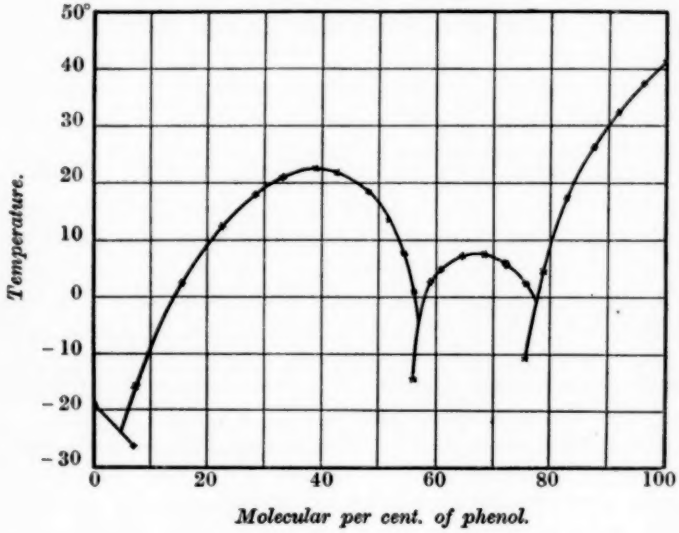
In a large number of the mixtures examined, freezing was started with difficulty, and frequently only after the temperature had been reduced to 20° or 30°, and in some cases as much as 50°, below the freezing point. In all such cases a preliminary determination of the freezing point was made, and then, a little of the solid phase having been prepared in a test-tube, the mixture was cooled to a

temperature a degree or so below the estimated freezing point and freezing started by inoculation with a crystal of the solid. In this way successive determinations of the freezing point of a mixture were made until the agreement obtained was within 0·1°.

All the substances used, with the exception of quinoline, were the same as those used in the viscosity experiments, and were redistilled before use. The quinoline was prepared by Skraup's synthetic process, and in addition to the usual purification by dis-

FIG. 1

Phenol and quinoline.



tillation was purified further by freezing out several times. In this way a pure product was obtained.

Phenol and Quinoline.

The freezing points of a number of mixtures of phenol and quinoline were determined, and particulars of these are given in table I. These results are shown graphically in Fig. 1, from which it will be seen that these two substances combine with each other in a rather unexpected manner; two compounds are formed which may be represented by the formulæ $(C_6H_6O)_2,(C_9H_7N)_3$ and

$$(C_6H_6O)_2,(C_9H_7N).$$

No indication of the compound naturally expected—one containing the two components in equimolecular proportions—was obtained.

There can be no doubt, however, from what we know of the acidic and basic nature of phenol and quinoline respectively that the equimolecular compound is present in the liquid mixture, and that, so far as the energy change is concerned, the formation of this compound is the main reaction. The existence of the two compounds indicated in the freezing-point diagrams is in all probability the result of a secondary reaction between the equimolecular compound and the two components much of the same kind as in the formation of salt hydrates. A more correct method of representing the formulæ of these two compounds is probably as follows:

$2\{(C_6H_6O)(C_9H_7N)\},(C_9H_7N)$ and $\{(C_6H_6O)(C_9H_7N)\},(C_6H_6O)$.

With some of the mixtures two freezing points were obtained, the first and lower one being the freezing point of the mixture with the liquid in unstable equilibrium with one solid phase, and the second and higher one being the freezing point of the mixture when the liquid was in stable equilibrium with another solid phase. Such pairs of freezing points are shown connected by a bracket in the tables.

There are three eutectics on the freezing-point diagram for this mixture. Each eutectic temperature was determined from two mixtures the compositions of which were near to but on opposite sides of that of the eutectic mixture itself. The mean of the two values thus obtained, which were always in close agreement, was taken as the eutectic temperature. The eutectics for this mixture are:

I.	At	5·0	molecular	per cent.	of Phenol.	Temp. −24·1°
II.	„	57·5	„	„	„	„ −4·6°
III.	„	77·6	„	„	„	„ −0·7°

TABLE I.

Mixtures of Phenol and Quinoline.

Weight of phenol in grams.	Weight of quinoline in grams.	Percentage of phenol.	Molecular percentage of phenol.	Freezing point.
0·00	34·20	0·00	0·00	−19·5°
1·90	„	5·26	7·06	−26·2 −15·8
4·65	„	11·97	15·70	2·5
7·31	„	17·61	22·65	12·0
9·81	„	22·29	28·20	18·0
12·30	„	26·44	33·00	20·9
15·17	„	30·73	37·80	22·4
18·36	„	34·93	42·35	21·6
23·14	„	40·34	48·20	18·45
26·96	„	44·10	51·70	13·55
30·09	„	46·80	54·65	7·5
36·22	„	51·42	59·20	−13·65 +2·5
29·84	31·61	48·55	56·35	−14·4 +1·0

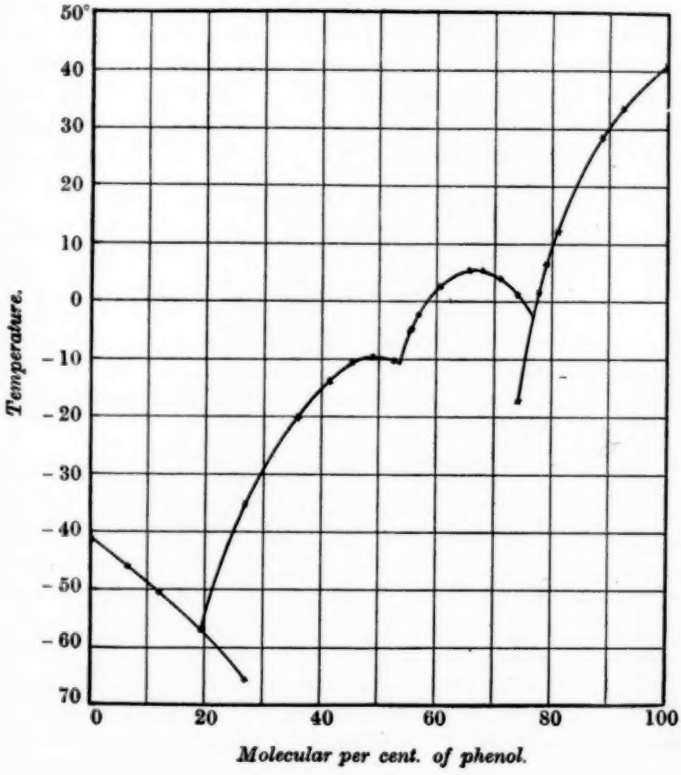
TABLE I. (*continued*).

Mixtures of Phenol and Quinoline.

Weight of phenol in grams.	Weight of quinoline in grams.	Percentage of phenol.	Molecular percentage of phenol.	Freezing point.
23·84	26·46	53·01	60·75	4·8
,,	22·32	57·22	64·65	7·0
,,	18·82	61·34	68·50	7·2
,,	15·84	65·31	72·00	5·8
,,	13·17	69·37	75·65	−10·8 +2·4
,,	10·97	73·11	78·75	4·55
,,	8·36	78·11	83·00	17·50
,,	5·79	83·75	87·65	26·25
,,	3·64	89·15	91·90	32·70
,,	1·645	94·79	96·20	37·30
,,	0·00	100·00	100·00	41·0

FIG. 2.

Phenol and pyridine.



Phenol and Pyridine.

Mixtures of these two substances were made up as before, and their freezing points determined. Particulars of these mixtures are given in table II., and Fig. 2 shows the results graphically.

TABLE II.

Mixtures of Phenol and Pyridine.

Weight of phenol in grams.	Weight of pyridine in grams.	Percentage of phenol.	Molecular percentage of phenol.	Freezing point.
0·00	30·89	0·00	0·00	−40·7°
2·62	„	7·82	6·66	−45·8
5·06	„	14·08	12·08	−50·3
8·68	„	21·94	19·12	−56·9
13·52	„	30·45	26·90	−65·7 −35·0
28·70	43·03	40·02	35·9	−20·2
„	35·05	45·03	41·15	−14·0
„	29·37	49·43	45·05	−10·8
„	25·17	53·27	48·9	−9·7
„	22·09	56·50	52·2	−10·2
„	18·26	61·10	56·9	−2·15
„	11·34	71·68	68·0	+5·4
„	8·42	77·32	74·15	−17·6 +1·3
„	6·88	80·67	77·75	1·7
„	5·74	83·43	81·0	12·0
„	2·02	93·44	92·3	33·5
„	0·00	100·00	100·0	41·0
26·41	2·86	90·24	88·7	28·6
„	5·81	81·96	79·3	6·55
„	9·08	74·42	70·9	4·0
„	11·62	69·29	65·5	5·4
„	14·54	64·51	60·45	2·5
„	17·87	59·65	55·4	−4·9

In this case the freezing-point diagram consists of four distinct branches; the two middle parts each contain a summit, thus two compounds are indicated. The summit at 50 molecular per cent. of phenol indicates the presence of a compound containing equimolecular proportions of phenol and pyridine, which may be represented by the formula $(C_6H_6O)(C_5H_5N)$. The other branch, which has a summit of 67 molecular per cent. of phenol, indicates the presence of a compound containing two equivalents of phenol to one of pyridine, which may be represented by the formula $(C_6H_6O)_2(C_5H_5N)$. The three eutectic points were determined as before, and found to be:

I. −57·0° at 19·2 molecular per cent. of phenol.
II. −10·8° at 53·7 „ „ „ „
III. −2·4° at 76·8 „ „ „ „

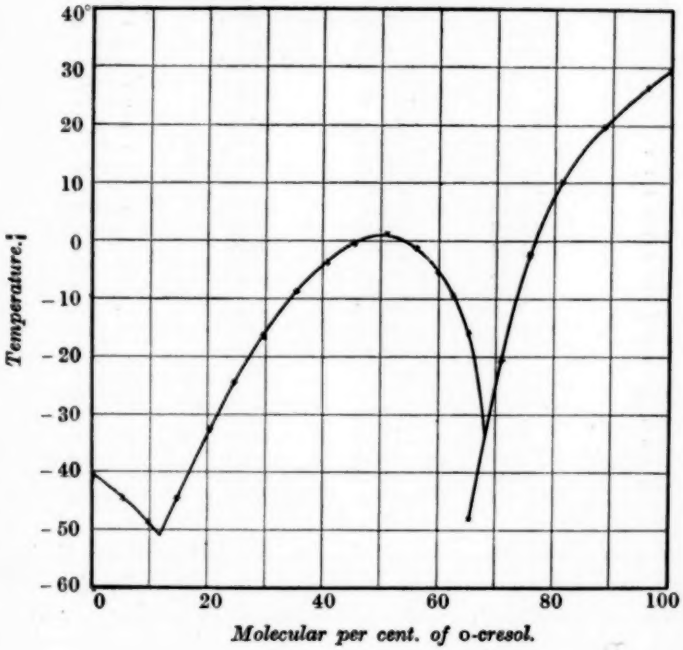
o-Cresol and Pyridine.

Experimental data obtained for mixtures of these two substances are given in table III, and represented graphically in Fig. 3.

As will be seen in the diagram, the freezing-point curve for this mixture consists of three branches, of which the middle one passes through a maximum at a point corresponding with a temperature

FIG. 3.

o-Cresol and pyridine.



of 1·3° and a composition of 50 molecular per cent. of *o*-cresol. This indicates the presence of one compound only containing equimolecular proportions of the two components. The two eutectics were found to be:

−50·95° at 11·9 molecular per cent. of *o*-cresol.
and −33·8° „ 68·2 „ „ „

TABLE III.

Mixtures of o-Cresol and Pyridine.

Weight of *o*-cresol in grams.	Weight of pyridine in grams.	Percentage of *o*-cresol.	Molecular percentage of *o*-cresol.	Freezing point.
0·00	29·00	0·00	0·00	−40·7°
2·225	„	7·13	5·33	−44·6
4·365	„	13·08	9·92	−48·9
6·69	„	18·75	14·43	−44·5
9·30	„	24·29	20·12	−32·45
13·07	„	31·06	24·5	−24·6
16·84	„	36·73	29·8	−16·7
21·68	„	42·78	35·45	−8·9
27·07	„	48·32	40·65	−3·9
32·83	„	53·10	45·3	0·0
31·08	22·03	58·52	51·0	1·2
„	17·99	63·34	55·9	−0·95
„	15·28	67·04	59·8	−5·2
22·41	10·09	68·96	62·4	−9·3
31·08	12·14	71·90	65·15	−48·1 −15·8
„	9·35	76·88	70·9	−20·7
„	7·22	81·16	75·75	−2·25
„	5·11	85·88	81·3	10·2
„	2·88	91·52	88·8	19·9
„	0·99	96·94	95·9	26·75
„	0·00	100·00	100·0	29·75

m-Cresol and Pyridine.

Mixtures of these two substances were examined in the same way as the others, but it was found impossible to obtain the freezing points throughout the whole range of composition. Mixtures containing between 42 and 80 per cent. of *m*-cresol could not be frozen; when cooled down they became so stiff that it was impossible to stir them, and when cooled in liquid air the mixture set into a glass-like solid. A mixture of approximately equimolecular proportions of the two components when cooled slowly with constant stirring and rubbing resisted all efforts to effect crystallisation. Details of the measurements obtained are given in table IV, and these are represented graphically in Fig. 4, curve I, from which obviously no conclusion can be drawn as to the formation of a compound, although there can be little doubt that a compound is formed.

FIG. 4.

I. *Phenol and dimethylaniline.*
II. m-*Cresol and pyridine.*

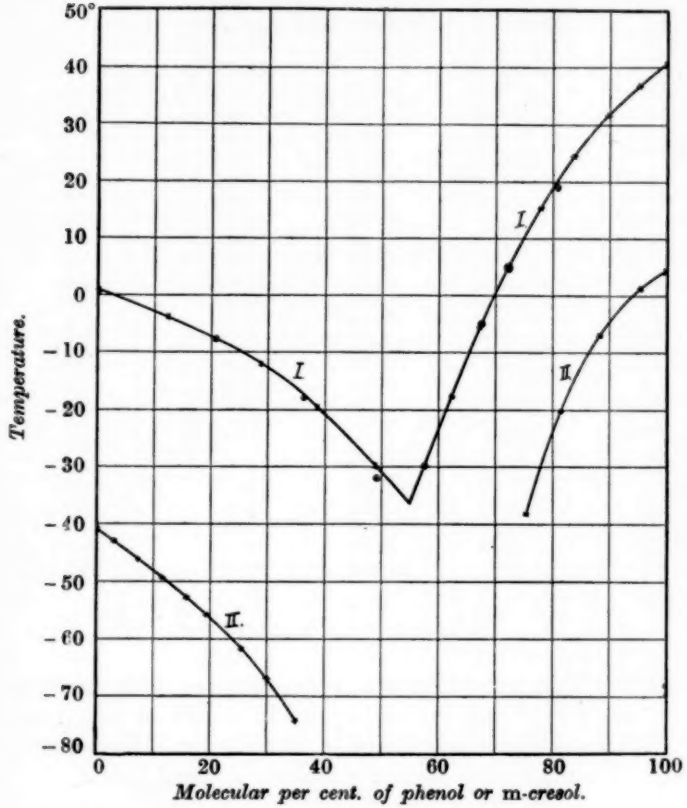


TABLE IV.

Mixtures of m-*Cresol and Pyridine.*

Weight of *m*-cresol in grams.	Weight of pyridine in grams.	Percentage of *m*-cresol.	Molecular percentage of *m*-cresol.	Freezing point.
0·00	28·20	0·00	0·00	−40·7°
1·32	,,	4·47	3·31	−43·0
3·05	,,	9·76	7·30	−45·9
4·99	,,	15·03	11·45	−49·05
7·10	,,	20·11	15·45	−52·7
9·39	,,	24·99	19·6	−55·6
12·96	,,	31·49	25·15	−61·5
16·46	,,	36·85	29·9	−67·0
20·06	,,	41·58	35·1	−74·5
31·16	7·40	80·81	75·5	−38·3
,,	5·165	85·78	81·5	−20·2
,,	3·035	91·14	88·3	− 7·1
,,	1·035	96·81	95·7	1·15
,,	0·00	100·00	100·0	4·5

p-*Cresol and Pyridine.*

Table V contains particulars of a number of mixtures of these two compounds with the corresponding freezing points, and Fig. 5 is a graphical representation of the data.

FIG. 5.

p-*Cresol and pyridine.*

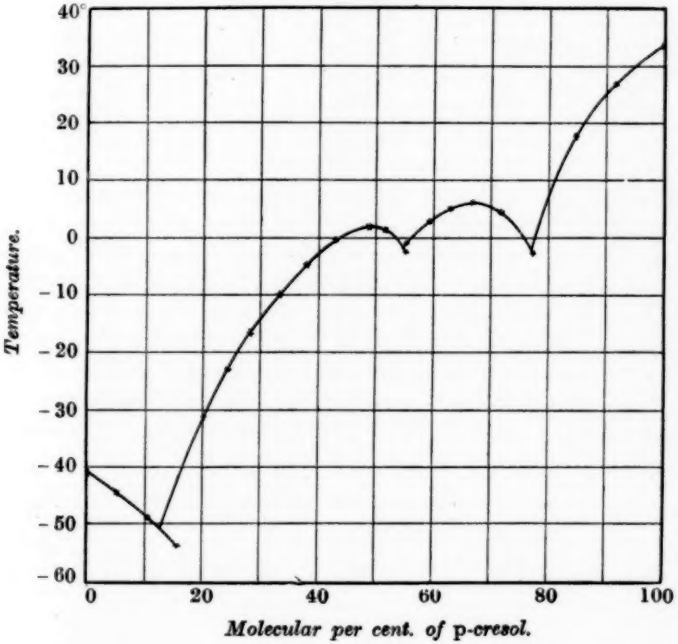


TABLE V.

Mixtures of p-*Cresol and Pyridine.*

Weight of *p*-cresol in grams.	Weight of pyridine in grams.	Percentage of *p*-cresol.	Molecular percentage of *p*-cresol.	Freezing point.
0·00	27·63	0·00	0·00	−40·7°
1·97	,,	6·66	4·96	−44·8
4·49	,,	13·98	10·61	−48·9
6·88	,,	19·94	15·42	−53·8
9·50	,,	25·60	20·10	−31·0
12·11	,,	30·47	24·30	−23·0
14·80	,,	34·88	28·15	−16·7
18·68	,,	40·33	33·10	−9·8
23·10	,,	45·53	37·97	−4·5
28·36	,,	50·65	42·85	−0·3
36·03	,,	56·59	48·90	2·0

TABLE V. (*continued*).

Mixtures of p-*Cresol and Pyridine.*

Weight of *p*-cresol in grams.	Weight of pyridine in grams.	Percentage of *p*-cresol.	Molecular percentage of *p*-cresol.	Freezing point.
30·66	21·05	59·29	51·6	1·4
,,	18·31	62·62	55·15	−2·4 −0·95
,,	15·45	66·49	59·3	2·6
,,	13·22	69·87	63·0	5·0
,,	11·05	73·52	67·0	6·2
,,	8·84	77·62	71·65	4·4
,,	6·65	82·19	77·2	−2·4
,,	4·03	88·39	84·75	17·85
,,	1·99	93·91	91·7	26·95
,,	0·00	100·00	100·0	33·8

The freezing-point curve for this mixture consists of four branches, and very closely resembles the one for mixtures of phenol and pyridine. The two summits at approximately 50 and 67 molecular per cent. of *p*-cresol show clearly that *p*-cresol and pyridine combine together to form two compounds: one, which melts at 2°, contains equimolecular proportions of the two components; the other, which melts at 6·2°, contains two molecular equivalents of *p*-cresol to one of pyridine. The formulæ representing these two compounds are $(C_7H_8O)(C_5H_5N)$ and $(C_7H_8O)_2(C_5H_5N)$ respectively. The three eutectic points for this mixture were found to be:

I. −50·8° at 12·8 molecular per cent. of *p*-cresol.
II. −1·4° ,, 55·0 ,, ,, ,,
III. −2·05° ,, 77·0 ,, ,, ,,

Aniline and o-*Chlorophenol.*

Details of the mixtures of these two substances with their corresponding freezing points are given in table VI, and these are represented graphically in Fig. 6.

It is obvious from the shape of the freezing-point curve that an equimolecular compound of these two substances is formed, and that it possesses considerable stability. The middle branch of this curve consists of an unusually large proportion of the whole; the melting point of the compound $(C_6H_5OCl)(C_6H_7N)$−, 29·4°, is considerably higher than that of either component. The two eutectic temperatures are −12·0° and −1·75°, and the corresponding mixtures contain 9·7 and 83·8 molecular per cent. of *o*-chlorophenol respectively.

FIG. 6.

o-Chlorophenol and aniline.

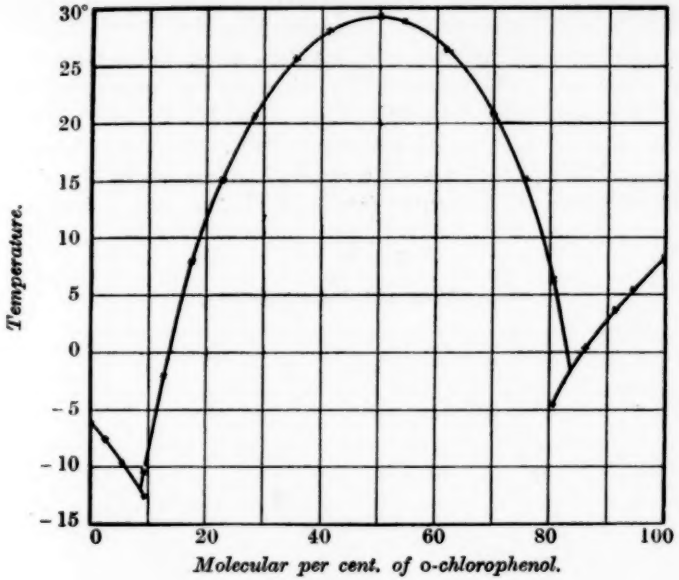


TABLE VI.

Mixtures of o-Chlorophenol and Aniline.

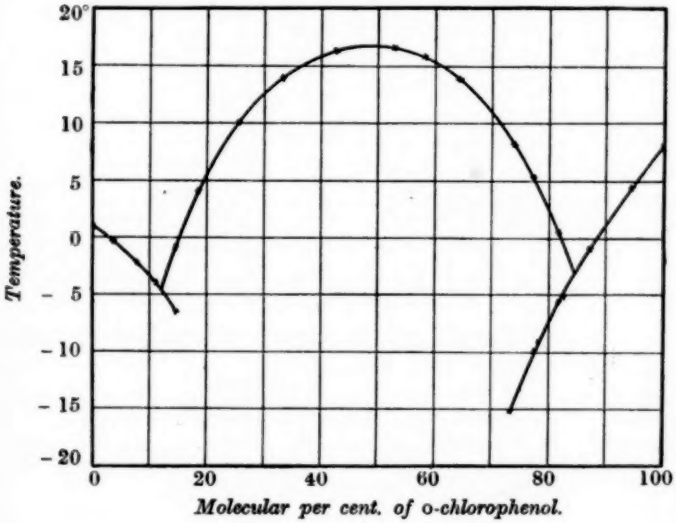
Weight of *o*-chloro-phenol in grams.	Weight of aniline in grams.	Percentage of *o*-chloro-phenol.	Molecular percentage of *o*-chloro-phenol.	Freezing point.
0·00	29·90	0·00	0·00	−6·5°
0·97	,,	3·15	2·30	−7·8
2·33	,,	7·23	5·35	−9·5
4·16	,,	12·21	9·15	−12·5 −10·4
5·89	,,	16·45	12·50	−2·0
8·65	,,	22·44	17·3	7·85
12·26	,,	29·08	22·9	15·15
16·69	,,	35·82	28·75	20·7
22·54	,,	42·99	35·35	25·65
29·31	,,	49·50	41·5	28·06
33·80	24·75	57·72	50·2	29·35
,,	20·60	62·13	54·25	28·95
,,	15·26	68·90	61·6	26·35
,,	10·64	76·05	69·65	20·85
,,	7·92	81·02	75·5	15·10
,,	5·77	85·41	80·5	−4·7 +6·2
,,	3·88	89·71	86·3	0·3
,,	2·29	93·65	91·45	3·9
,,	1·095	96·85	94·35	5·45
,,	0·00	100·00	100·00	8·0

o-Chlorophenol and Dimethylaniline.

The freezing-point curve of mixtures of phenol and dimethylaniline has been determined by Kremann (*Monatsh.*, 1906, **27**, 91), but his results failed to indicate the formation of a compound between these two substances. The viscosity measurements for mixtures of phenol and dimethylaniline described in Part I. gave some indication of the formation of compounds. The substitution of *o*-chlorophenol for phenol caused a marked difference in the shape of the viscosity-composition curve (see Part II., *loc. cit.*), a difference

FIG. 7.

o-Chlorophenol and dimethylaniline.



which was attributed to the more extensive formation of compounds between the two components of the mixture. If these deductions are correct, the probability of a solid compound separating from the liquid mixture when the latter is cooled sufficiently will be greater in the cases of the *o*-chlorophenol mixtures than in the corresponding mixtures containing phenol.

Mixtures of *o*-chlorophenol and dimethylaniline were made up in the usual way and their freezing points determined. The experimental data are given in table VII, and represented graphically in Fig. 7.

TABLE VII.

Mixtures of o-Chlorophenol and Dimethylaniline.

Weight of *o*-chloro-phenol in grams.	Weight of dimethyl-aniline in grams.	Percentage of *o*-chloro-phenol.	Molecular percentage of *o*-chloro-phenol.	Freezing point.
0·00	33·15	0·00	0·00	1·0°
1·29	„	3·75	3·53	−0·35
2·85	„	7·92	7·45	−2·2
4·36	„	11·61	10·95	−4·0
6·07	„	15·45	14·60	−6·65 −1·00
7·97	„	19·37	18·4	4·0
12·02	„	26·61	25·4	10·0
17·93	„	35·10	33·6	13·75
26·74	„	44·64	42·5	16·2
40·44	34·53	53·94	52·45	16·6
„	27·21	59·78	58·2	15·7
„	21·30	65·49	64·05	13·9
„	13·48	74·99	73·8	−15·1 +8·1
„	8·45	82·71	81·8	−5·5 +0·4
31·15	„	78·66	77·5	−9·8 +5·3
42·69	5·82	88·00	87·3	−1·0
„	2·43	94·61	94·3	4·5
„	0·00	100·00	100·0	8·0

The freezing-point curve for this mixture consists of three branches. There is a summit on the middle branch, at 50 molecular per cent. of *o*-chlorophenol, indicating the presence of a compound consisting of equimolecular proportions of the two components. The melting point of this compound is 16·7°, but it is obvious from the flat shape of the curve in the neighbourhood of the maximum point that a considerable amount of dissociation takes place when the compound is melted. It will be observed, on comparing Figs. 6 and 7 that the maximum on the *o*-chlorophenol–aniline curve is much sharper than the other, an indication that the compound of *o*-chlorophenol and aniline is less dissociated on melting than the dimethylaniline compound is, although the melting point of the former is considerably higher than that of the latter. This is exactly as was expected, since the salt-forming property of dimethylaniline is well known to be much less than that of aniline. Nevertheless, by substituting the more strongly acid *o*-chlorophenol for phenol in the mixtures containing dimethylaniline, compound formation has been so far increased as to produce a large middle branch on the freezing-point curve.

Phenol and Dimethylaniline.

As already stated, the freezing-point curve for this mixture has been determined by Kremann (*loc. cit.*), who was only able to obtain two branches. Kremann states, however, that mixtures of these two substances containing between 50 and 67 molecular per cent. of phenol could not be made to solidify. It has previously been mentioned that measurements of viscosity, made with mixtures of these two substances, gave some indication of the presence of a compound. The question, therefore, as to whether the complete freezing-point curve for mixtures of these two substances should consist of three branches remained unsettled, and, on account of its importance from the point of view of the interpretation of the viscosity results, it was considered advisable to repeat Kremann's work on this mixture. Mixtures of the two substances were made up in the usual way and their freezing points determined. As will be seen in table IV*a*, which contains particulars of the mixtures made and their freezing points, it was found possible to obtain the whole of the curve, the eutectic temperature being determined quite definitely from mixtures containing both less and more phenol than the eutectic mixture itself. These results are shown graphically in Fig. 4. The points obtained by Kremann are indicated by circles on this diagram. The whole of the freezing-point curve for this mixture consists of two branches only, which start from the freezing points of the pure substances and meet at the eutectic point; this eutectic temperature was found to be $-36{\cdot}0°$, and the composition of the mixture is such as to contain 54·8 molecular per cent. of phenol.

Knowing what we do about the acidic and basic properties of phenol and dimethylaniline respectively, it is inconceivable that a homogeneous liquid mixture of these two substances, when cooled to a temperature below $-30°$, contains no compound. This is an example in which the freezing-point curve fails to give conclusive evidence as to the existence or otherwise of a compound in a mixture. A very similar case has been mentioned by Philip (*loc. cit.*), who observed that a mixture of *o*-nitrophenol and *p*-toluidine in the liquid state has a deep red colour, which, in the case of nitro-compounds, is generally regarded as indicative of compound formation, yet the freezing-point curve consists of two branches only and a single eutectic.

TABLE IV*a*.

Mixtures of Phenol and Dimethylaniline.

Weight of phenol in grams.	Weight of dimethyl-aniline in grams.	Percentage of phenol.	Molecular percentage of phenol.	Freezing point.
0·00	27·00	0·00	0·00	1·0°
2·95	,,	9·85	12·30	−3·6
8·35	,,	23·68	28·55	−12·0
13·06	,,	32·60	38·4	−19·4
20·22	,,	42·90	48·7	−29·7
31·95	30·48	51·18	57·3	−29·5
,,	24·95	56·16	62·2	−17·8
,,	20·09	61·41	67·25	−5·5
,,	15·89	66·79	72·05	4·85
,,	11·76	73·10	77·7	15·1
,,	7·95	80·07	83·7	24·4
,,	4·70	87·18	89·9	31·8
,,	2·11	93·80	95·25	36·85
,,	0·00	100·00	100·00	40·8

Phenol and Diphenylmethylamine.

The freezing-point curve for mixtures of phenol and diphenylamine has been determined by Philip (*loc. cit.*), who found that it consisted of two simple branches meeting at a eutectic point. There was no reason to suppose that the freezing-point curve of mixtures of phenol and diphenylmethylamine would be of a different character, but, on account of the uncertainty attached to these things and also to make the work more complete, it was decided to determine the freezing-point curve for mixtures of these two substances. The experimental figures are given in table VIII, and the results are shown graphically in Fig. 8.

TABLE VIII.

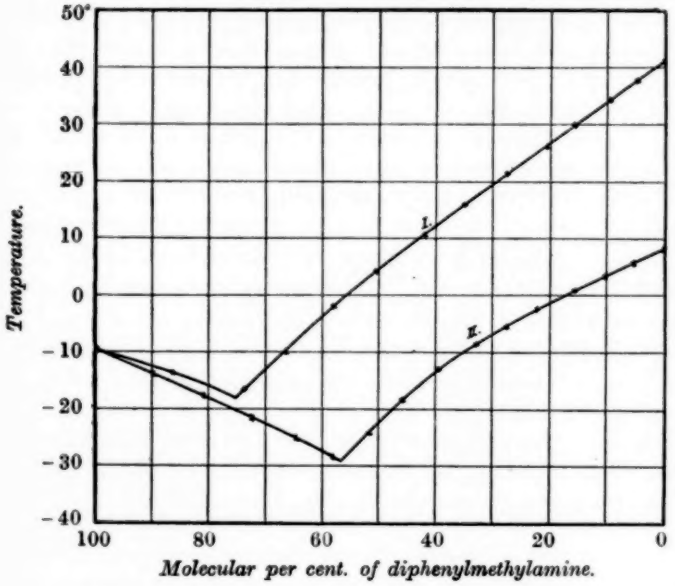
Mixtures of Phenol and Diphenylmethylamine.

Weight of phenol in grams.	Weight of diphenyl methyl-amine in grams.	Percentage of phenol.	Molecular percentage of phenol.	Freezing point.
0·00	31·60	0·00	0·00	−9·6°
2·54	,,	7·45	13·54	−13·4
5·79	,,	15·48	26·27	−16·5
8·28	,,	20·75	23·75	−9·6
11·73	,,	27·10	42·0	−2·0
15·89	,,	33·5	49·5	4·0
22·45	,,	41·5	58·0	10·6
30·17	,,	48·8	65·0	16·0
32·02	23·67	57·5	72·5	21·6
,,	11·61	73·4	84·3	30·3
,,	3·18	91·0	95·3	38·0
,,	0·00	100·0	100·0	41·0

The freezing-point curve for this mixture consists, as was expected, of two simple branches which start from the freezing points of the two pure components and meet at a eutectic point. The temperature of this eutectic was found to be $-18{\cdot}1°$, and the eutectic mixture, according to the curve, contains 25·0 molecular per cent. of phenol. The occurrence of the eutectic point at this simple molecular proportion is quite accidental, and, as has repeatedly been

FIG. 8.

I. *Phenol and diphenylmethylamine.*
II. o-*Chlorophenol and diphenylmethylamine.*



pointed out, is no indication of the formation of a compound of that composition.

o-*Chlorophenol and Diphenylmethylamine.*

The substitution of *o*-chlorophenol for phenol in mixtures containing dimethylaniline caused the freezing-point curve of the mixture to change from the simplest type of two branches meeting at a eutectic point to one of three branches, of which the middle one passes through a maximum indicative of compound formation, and meets the other two, which start at the freezing points of the pure substances at two eutectic points. Although the viscosity measurements made with mixtures of *o*-chlorophenol and diphenylmethylamine described in Part II. (this vol., p. 449) show no

evidence of compound formation, it was thought advisable to determine the freezing-point curve of this mixture in order to ascertain whether the substitution of *o*-chlorophenol for phenol itself would produce the same kind of alteration in the type of curve for this mixture as that just mentioned.

Experimental figures are given in table VIII*a* for mixtures of *o*-chlorophenol and diphenylmethylamine, and the results are shown graphically in Fig. 8, curve II, from which it will be seen that the freezing-point curve for this mixture is of the same type as the last, namely, two branches only, meeting in one eutectic. This eutectic temperature was found to be −29·1°, and the corresponding mixture contains 43·6 molecular per cent. of *o*-chlorophenol.

So far as the freezing-point curves indicate, there is no evidence of the formation of a compound in either of the mixtures containing diphenylmethylamine.

TABLE VIII*a*.

Mixtures of o-Chlorophenol and Diphenylmethylamine.

Weight of *o*-chlorophenol in grams.	Weight of diphenylmethylamine in grams.	Percentage of *o*-chlorophenol.	Molecular percentage of *o*-chlorophenol.	Freezing point.
0·00	30·65	0·00	0·00	−9·6°
2·40	,,	7·27	10·04	−13·6
5·02	,,	14·10	18·94	−17·6
8·30	,,	21·30	27·83	−21·6
11·63	,,	27·55	35·14	−25·1
15·79	,,	34·00	42·33	−28·5
20·37	,,	39·90	48·60	−24·2
25·44	,,	45·40	54·20	−18·7
33·52	31·24	51·75	60·43	−13·0
,,	23·43	58·85	67·08	−8·8
,,	13·16	71·70	78·29	−2·15
,,	5·43	86·05	89·78	3·4
,,	0·00	100·00	100·00	8·0

o-Chlorophenol and Quinoline.

It has already been shown in Part II. (*loc. cit.*) that mixtures of these two substances are extremely viscous at low temperatures. This, no doubt, has some connexion with the persistence with which this mixture remains in the liquid state on cooling. Some idea of the difficulty with which this substance freezes may be obtained from the fact that the whole of the measurements of the viscosities and densities of these mixtures described in Part II., which include a set at 0°, were obtained without any of the mixtures freezing. It was necessary to inoculate most of these mixtures with a crystal of the solid in order to start crystallisation. Numerical details of the experiments are given in table IX, and these are represented graphically in Fig. 9.

FIG. 9.

o-Chlorophenol and quinoline.

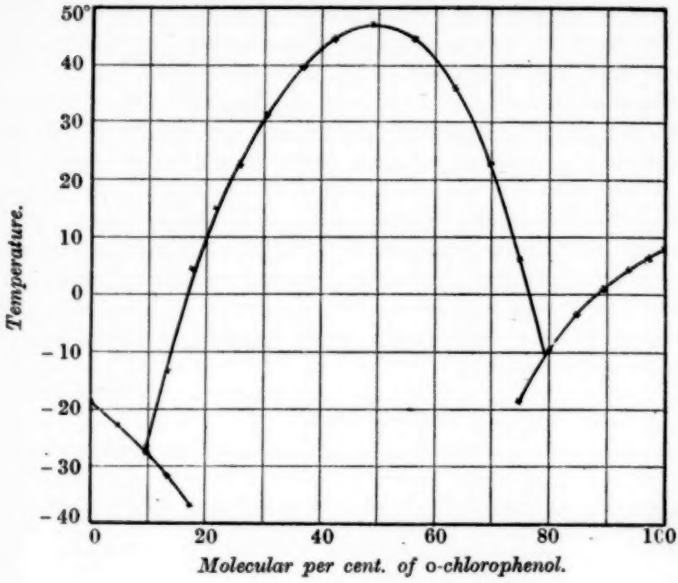


TABLE IX.

Mixtures of o-Chlorophenol and Quinoline.

Weight of *o*-chloro-phenol in grams.	Weight of quinoline in grams.	Percentage of *o*-chloro-phenol.	Molecular percentage of *o*-chloro-phenol.	Freezing point.
0·00	31·55	0·00	0·00	−19·5°
1·47	,,	4·45	4·46	−23·0
3·35	,,	9·58	9·62	−27·6 −26·6
4·77	,,	13·13	13·18	−31·5 −13·2
6·53	,,	17·15	17·20	−36·9 +4·5
7·76	28·60	21·34	21·4	15·0
9·84	,,	25·60	25·7	22·4
12·42	,,	30·27	30·35	31·5
16·44	,,	36·51	36·6	39·5
20·70	,,	42·00	42·1	44·45
27·23	,,	48·78	48·9	47·35
36·29	,,	55·93	56·05	44·75
35·48	20·58	63·28	63·35	36·0
,,	15·45	69·66	69·7	22·8
,,	11·96	74·78	74·8	−18·9 +6·0
,,	8·96	79·82	79·85	−9·9
,,	6·40	84·72	84·75	−3·4
,,	4·21	89·39	89·4	0·7
,,	2·41	93·65	93·65	4·25
,,	1·07	97·07	97·07	6·25
,,	0·00	100·00	100·00	8·0

The two eutectic points were:

I. −27·6° at 9·6 molecular per cent. of *o*-chlorophenol.
II. −10·9° „ 79·1 „ „ „

The central branch of the freezing-point curve for mixtures of *o*-chlorophenol and quinoline has a summit which reaches its highest point at 50 molecular per cent., indicating the presence of a compound containing equimolecular proportions of the two components. The melting point of this compound is 47·4°.

o-Chlorophenol and Pyridine.

Experimental details of the composition and freezing points of a number of mixtures of these two substances are given in table X, and these results are shown graphically in Fig. 10.

TABLE X.

Mixtures of o-Chlorophenol and Pyridine.

Weight of *o*-chloro-phenol in grams.	Weight of pyridine in grams.	Percentage *o*-chloro-phenol.	Molecular percentage of *o*-chloro-phenol.	Freezing point.
0·00	30·05	0·00	0·00	−40·7°
2·69	„	8·22	5·22	−44·5
5·95	„	16·53	10·87	−49·8
9·48	„	23·98	16·32	−55·4
13·86	„	31·56	22·2	−61·4
27·31	42·65	39·04	28·3	−48·1
„	35·22	43·68	32·3	−40·0
„	27·85	49·50	37·65	−31·5
22·57	19·53	53·62	41·5	−26·45
27·31	„	58·33	46·3	−22·5
33·78	20·40	62·34	50·5	−21·7
36·73	„	64·31	52·6	−22·6
40·61	„	66·56	54·0	−23·3
46·57	„	69·55	58·5	−62·0 −27·8
33·78	10·18	76·83	67·1	−38·5 −34·5
34·10	5·79	85·49	78·4	−12·3
„	3·77	90·05	84·8	−4·1
„	2·21	93·93	90·5	2·2
„	1·065	97·01	95·2	5·9
„	0·00	100·00	100·0	8·0

The freezing-point curve for mixtures of these two substances consists of three branches, of which the middle one has a well-marked summit at 50 molecular per cent. of *o*-chlorophenol. This indictes the presence of a compound consisting of equimolecular proportions of the two components and having a melting point of −21·6°. The two eutectic points on this curve were found to have the following temperatures and concentrations, the latter being read off the curve:

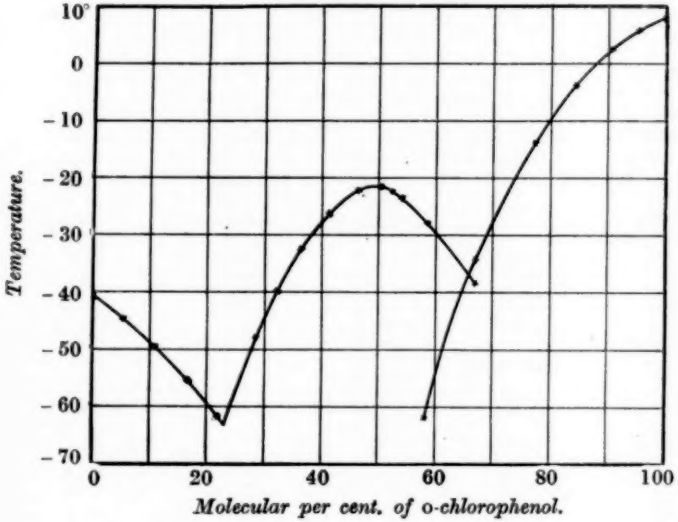
I. −63·0° at 23·1 molecular per cent. of *o*-chlorophenol.
II. −36·9° „ 66·1 „ „ „

o-Chlorophenol and Acetone.

The theory has been put forward from time to time that all chemical reactions are preceded by the formation of more or less unstable additive compounds, but it has only been possible in a relatively few cases to isolate the intermediate additive compounds. It is well known that acetone forms condensation products with a number of organic substances, amongst which are phenols, and it has been shown by Schmidlin and Lang (*Ber.*, 1910, **43**, 2806) that the reactions between acetone and this last class of substances are amongst those in which the intermediate additive compounds

FIG. 10.

o-Chlorophenol and pyridine.



are sufficiently stable to allow of their being isolated. In this case the formation of the additive compound takes place immediately on mixing the phenol with acetone, whilst the second part of the reaction, the true condensation, only takes place when the reaction mixture is brought into contact with the condensing agent.

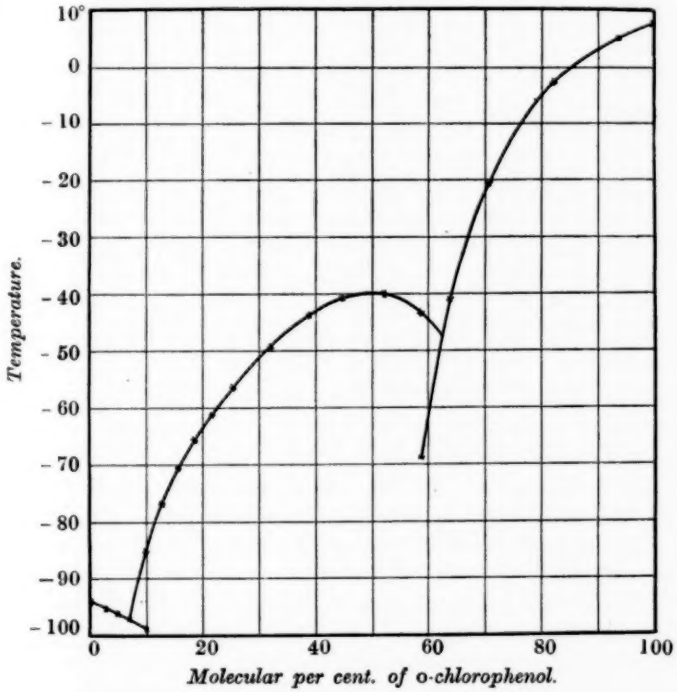
Schmidlin and Lang isolated additive compounds of acetone with phenol, resorcinol, quinol, catechol, and pyrogallol, but found that the relative amounts of the components in the additive compound are not always the same as the relative proportions in which they react to form the condensation product. It appears, therefore, that although acetone might be expected to combine with *o*-chlorophenol,

the relative proportions of the two components in the additive product cannot be predicted with certainty. The inflected viscosity curves for mixtures of these two substances described in Part I. are also suggestive of the formation of compounds. It was decided, therefore, to determine the freezing-point curve for this mixture with the hope of obtaining more definite information on this subject.

Table XI contains the experimental figures for the mixtures of

FIG. 11.

o-Chlorophenol and acetone.



acetone and *o*-chlorophenol and their freezing points, and Fig. 11 shows these results graphically. It will be seen that there are three distinct branches in the freezing-point curve. The middle branch, which contains a well-defined summit at 50 molecular per cent. of *o*-chlorophenol, is a clear indication of the formation of a compound containing equimolecular proportions of the two constituents. The melting point of this compound is $-39{\cdot}8°$. The two eutectic points at which the middle branch intersects the other two branches of the freezing-point curve were found to have the tem-

peratures $-97{\cdot}1°$ and $-47{\cdot}6°$, and the compositions of the corresponding mixtures, as determined from the diagram, are 7·2 and 62·4 molecular per cent. of *o*-chlorophenol respectively.

TABLE XI.

Mixtures of o-Chlorophenol and Acetone.

Weight of *o*-chloro-phenol in grams.	Weight of acetone in grams.	Percentage of *o*-chloro-phenol.	Molecular percentage of *o*-chloro-phenol.	Freezing point.
0·00	28·20	0·00	0·00	−94·0°
1·70	,,	5·68	2·65	−95·0
3·07	,,	9·82	4·68	−96·0
4·82	,,	14·60	7·12	−97·0
6·82	,,	19·47	9·81	−84·8
9·02	,,	24·24	12·62	−76·9
11·48	,,	28·95	15·55	−70·6
14·24	,,	33·55	18·55	−65·7
17·32	,,	38·05	21·7	−61·2
21·15	,,	42·86	25·35	−56·3
29·43	,,	51·06	32·0	−49·6
33·53	23·77	58·51	38·85	−44·3
,,	18·76	64·12	44·6	−40·7
,,	13·81	70·81	52·2	−40·0
,,	10·76	75·70	58·45	−69·0 −43·1
,,	8·57	79·64	63·8	−41·1
,,	6·31	84·16	70·5	−20·6
,,	3·36	90·88	81·8	−2·9
,,	1·27	96·34	93·4	5·3
,,	0·00	100·00	100·0	8·0

Discussion of Results.

A comparison of the results obtained from freezing-point measurements with those deduced from measurements of viscosity leads to definite conclusions in some cases, whilst in others there is still some ambiguity.

In such mixtures as aniline and *o*-chlorophenol, and quinoline and *o*-chlorophenol, both viscosity and freezing-point curves point undoubtedly to the same conclusion, namely, the formation of a compound containing equimolecular proportions of the two components. The freezing-point curves for mixtures of phenol with aniline and *p*-toluidine have been determined by Schreinemakers (*loc. cit.*) and by Philip (*loc. cit.*) respectively, and these leave no room for doubt as to the manner in which these two bases combine with phenol, but if the viscosity curves for these two mixtures be considered for one temperature only, especially if that be a low one, compound formation is certainly indicated, but any deduction as to the composition of the compound, based on the position of maximum viscosity, or the maximum deviation from the calculated

mean, would lead to erroneous results. If, however, the viscosity measurements over a wide range of temperature be considered, the manner in which the position of maximum deviation of the viscosity from the calculated mean approaches asymptotically the ordinate corresponding with equimolecular proportions of the two components with rise in temperature, points to the formation of the same equimolecular compound. It should be stated, however, that deductions made from viscosity measurements are by no means as convincing, as regards the composition of the compound, as the indications of the freezing-point curves.

That phenol and quinoline form two compounds is clearly shown by the freezing-point curve, but it cannot be said that the viscosity measurements give any indication of either of them. The shape of the viscosity curves certainly does indicate compound formation, but, judging again by the inclination of the maximum viscosity–deviation–temperature curve—the small curve inset in the diagram of viscosities—the compound formed by these two substances should be one containing equimolecular proportions of the two constituents. This is a case where the indications of the viscosity measurements are possibly more truthful, as regards the liquid mixture, than the freezing-point curve, for it is quite possible that the compounds indicated by the latter exist only in the solid state, and dissociate on melting into the equimolecular compound and the free component.

At sufficiently low temperatures the viscosity curves for mixtures of pyridine with *m*- and *p*-cresols show no indication whatever of the formation of compounds. At higher temperatures they resemble the viscosity curves for mixtures of pyridine with phenol and *o*-cresol, and begin to show signs of compound formation; it cannot be claimed, however, that any definite inference as to the composition of the compound can be drawn from the viscosity curves for these mixtures. The freezing-point curves for mixtures of pyridine with phenol and *p*-cresol indicate the formation of two compounds in each case, but here, again, the viscosity curves are not undulating, as might be expected. The same conclusion must be drawn with regard to these mixtures as was arrived at by English and Turner (T., 1915, **107**, 774), who studied the freezing-point curves of mixtures of formamide with water and the aliphatic acids. It was found that some of these mixtures yield two compounds, but the corresponding viscosity curves, which had previously been determined by Merry and Turner (T., 1914, **105**, 748) gave no more than a qualitative indication of compound formation; they gave no indication of the presence of two compounds.

Mixtures of dimethylaniline and phenol provide an example in

which viscosity measurements indicate the formation of compounds and the freezing-point curve does not. Another example of the same kind is the following: The freezing-point curve for mixtures of antimony tribromide and triphenylmethane has been determined by Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1805), who found that it consists of two branches only, which meet at a eutectic point. The viscosity curve for this mixture has recently been determined by Kurnakov, Krotkov, and Oksman (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 558), who found that not only are the viscosities greater than the calculated means, but the curve actually contains a maximum, thus indicating compound-formation when the freezing-point curve failed to do so.

The substitution of *o*-chlorophenol for phenol in mixtures containing dimethylaniline resulted in a freezing-point curve having three branches, of which the middle one indicates the presence of a compound containing equimolecular proportions of the two components. The viscosity curve for this mixture at 0° contains a fairly high maximum, which is an indication of more extensive compound formation than in the case of the corresponding mixture containing phenol.

With regard to the mixtures containing acetone, the freezing-point curves give a definite indication of the formation of additive compounds of this substance with both phenol and *o*-chlorophenol, but the viscosity curves for the acetone–phenol mixture show no signs of the presence of a compound. A similar example has been described by English and Turner (*loc. cit.*), who found that water and formamide form a compound containing equimolecular proportions of the two components, but the viscosity curve for this mixture, which was determined by Merry and Turner (*loc. cit.*), is a sagged one. It is worthy of notice, however, that, judging from English and Turner's diagram, very little of the compound is present at a temperature of $-30°$ to $-40°$, and it is very questionable whether there is any of it at all at 25° and 40°; the temperatures at which Merry and Turner made their viscosity measurements. This, in addition to the influence of molecular association in the water molecules, would lead one to expect a sagged viscosity curve for this mixture. Another example of this type, which appears to be less doubtful than the water–formamide one, is a mixture of naphthalene and 1:3:5-trinitrobenzene. The freezing-point curve of this mixture was determined by Kremann (*Monatsh.*, 1904, **25**, 1215), who found that it contained three branches. Of these, the middle one, which is by far the largest, covering as it does the range from 8 to 88 per cent. of naphthalene, indicates the

formation of a compound consisting of equimolecular proportions of the two components. Kurnakov, Krotkov, and Oksman (*loc. cit.*) determined the viscosities of a number of mixtures of these two substances, and found that the curve connecting viscosity and composition is a sagged one. These investigators contend that the compound indicated by Kremann's freezing-point diagram exists only in the solid state, dissociation taking place on fusion. The summit of the freezing-point curve is certainly very flat, but it seems scarcely credible to the present author that there is complete dissociation at 152°, which is the temperature at which the viscosity measurements were made, and is only 1° above the melting point of the compound. The mixture of naphthalene and *m*-dinitrobenzene has been studied by the same investigators, and in this case the summit of the middle branch of the freezing-point curve, which indicates the formation of an equimolecular compound, is quite as flat as in the former case, but the viscosity curve for this mixture, at least the middle portion of it for a temperature just above the melting point of the compound, is not sagged, but concave towards the composition axis. At 90° the viscosity curve for this mixture is sagged.

Mixtures of acetone and *o*-chlorophenol form a compound containing equimolecular proportions of the two constituents, and it will be shown in Part IV. that there can be no question about the existence of this compound in the liquid mixture at a temperature far above its melting point. The inflection of the viscosity curve suggests compound formation, but no more. Another example of this kind is the mixture of antimony trichloride and benzene, which has been shown by Menschutkin to form a compound having the formula $2SbCl_3,C_6H_6$. Kurnakov, Krotkov, and Oksman found that the viscosity curve for this mixture was an inflected one resembling very closely those for acetone and o-chlorophenol.

Mixtures of phenol with diphenylamine and diphenylmethylamine and of the latter substance with *o*-chlorophenol exhibit no signs of compound formation when examined either by the freezing-point method or by the viscosity method.

It appears, therefore, that there are cases in which compound formation is indicated by viscosity measurements, and not by freezing-point curves, and, on the other hand, there are examples in which compound formation is proved by the shape of the freezing-point diagrams, yet not suggested by the viscosity curves. In the majority of cases, however, where the freezing-point diagram shows no sign of a compound, the viscosity curve falls below the straight line representing the calculated means; and where com-

pound formation is shown by the freezing-point curve, the viscosity curve lies partly or wholly above the straight line joining the viscosities of the two pure components.

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XXXVIII.—*The Study of Binary Mixtures. Part IV. Heats of Reaction and Specific Heats.*

By ARTHUR BRAMLEY.

ON many of the viscosity curves for binary mixtures there is a well-defined maximum which, as has already been shown, is not generally situated at a point corresponding with equimolecular proportions of the two components. As a rule, the maximum points are more marked the lower the temperature, and in some of the cases described in Part II. (this vol., p. 434), in which *o*-chlorophenol is a constituent of the mixture, the curvature at the summit of the curve is so large for the lower temperatures, and increases so rapidly as the temperature falls, as to suggest that the viscosity curves would rise to a definite peak if measurements could be made at a sufficiently low temperature.

It was pointed out in Part I. (this vol., p. 10) that it was preferable to consider the point on the viscosity curve which differed most from the calculated mean rather than the maximum point itself, but there are obviously many cases in which these two points are very nearly, if not actually, coincident, as, for example, where the maximum is fairly sharp or where the viscosities of the two components do not differ much. These maximum points are not only situated in positions away from the ordinate of equimolecular proportions, but, what is of more importance, they depart more and more from this position as the maximum becomes higher and more acute. This is especially noticeable in mixtures of *o*-chlorophenol with pyridine and dimethylaniline, described in Part II. (*loc. cit.*).

The many attempts that have been made from time to time to ascertain, from the position of maximum points on viscosity curves, the composition of the compounds formed between the two components of binary mixtures have generally led to results at variance with the more trustworthy deductions drawn from freezing-point diagrams. There are, however, a number of cases in which the

maximum on the viscosity curve is independent of the temperature at which this property is measured, and occurs, moreover, with that mixture which contains the two components in the same molecular proportion as the compound which they are known to form.

Kurnakov and his collaborators have described several mixtures of the type just mentioned, of which mixtures of alkylthiocarbimides with a number of organic bases studied by Kurnakov and Schemtschuschny (*Zeitsch. physikal. Chem.*, 1913, **83**, 481) and Kurnakov and Kviat (*ibid.*, 1914, **88**, 401) are examples.

There is, however, an important difference between binary mixtures which have continuous viscosity curves, such as those described by the present author in Parts I. and II. (*loc. cit.*), and those mentioned above, in which the viscosity curves consist of two distinct branches, both convex towards the axis of composition and meeting in a cusp. The reaction between the components of the latter class of mixtures proceeds to completion, and may be represented by the equation:

$$A + B = AB,$$

whereas the equilibrium between those mixtures studied by the writer which contain compounds is a balanced one, and should be represented by an equation of the type:

$$A + B \rightleftarrows AB.$$

That there appears to be a great tendency for the viscosity curves of some of the mixtures containing o-chlorophenol described in Part II. to approach the type characteristic of the irreversible mixtures mentioned above, raises the question again as to whether the position of a high and sharply rounded maximum on the viscosity curve of such a mixture as *o*-chlorophenol and pyridine, especially at low temperatures, is not indicative of the composition of some compound in the mixture. The fact that the position of such a maximum point does not correspond with the same simple molecular proportion of the mixture as is required by the compound proved by the freezing-point curve, or, indeed, with any simple molecular proportion at all, does not exclude the possibility of its revealing the presence of some other compound not indicated by the freezing-point diagram. Take, for example, the mixture of *o*-chlorophenol and pyridine. The viscosity curve for 0° rises to a very high and sharply rounded maximum at a point corresponding with about 80·5 per cent. of *o*-chlorophenol or a molecular percentage of very nearly 73. The freezing-point diagram for this mixture indicates the formation of only one compound containing 50 molecular per cent. of each component. Is it not possible, in view of the results obtained by Kurnakov and his collaborators, that this mixture, in the liquid state, might contain

a compound of the composition $(C_6H_5OCl)_3,C_5H_5N$? The question is not to be disposed of lightly.

The realisation of considerable lengths of freezing-point curves in the metastable regions shows the possibility of the existence of compounds in a liquid mixture which might escape detection by freezing-point or solubility methods. Roozeboom, in his classical experiments on the hydrates of ferric chloride, obtained sufficient of the metastable curves for the solubility of the dodecahydrate and the pentahydrate to realise the metastable eutectic point where these two curves intersect. Thus, a complete solubility curve for this system might have been obtained without detecting the existence of the heptahydrate. There is, of course, the other side of the question; the failure of a certain compound to crystallise out of a mixture may be because the formation of that compound has not taken place in the liquid phase. This appears to be the view taken by Kurnakov, Krotkov, and Oksman (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 558), who state that mixtures of naphthalene with some nitro-derivatives of benzene form compounds which exist only in the solid state, dissociation taking place on melting.

Since freezing-point measurements only give definite information as regards compounds which separate from a mixture in the solid state, there is still a considerable amount of uncertainty as regards the condition of binary mixtures in the liquid state, and on account of the apparently contradictory evidence obtained from viscosity curves and freezing-point diagrams for some of the mixtures described in Parts I. and II. (*loc. cit.*) and in Part III. (this vol., p. 469), it seemed desirable to obtain further knowledge, from an independent source if possible, regarding the constitution of these mixtures in the liquid state. This was the primary object of the work to be described in this section.

The specific heats of a number of binary liquid mixtures have been determined by A. Schultze (*Ber., Deut. physikal. Ges.*, 1912, **14**, 189, 258, 344; *Zeitsch. physikal. Chem.*, 1914, **86**, 309); by Schultze and Hock (*ibid.*, 1914, **86**, 445), and by Dolezalek and Schultze (*ibid.*, 1913, **83**, 45), and the general conclusions arrived at as a result of these investigations are as follows:

(1) The specific heat of a liquid mixture of two indifferent substances, neither of which contains associated molecules, is very approximately equal to the calculated mean value.

(2) When one or both of the components of a binary liquid mixture contains associated molecules and no additive compound is formed, the specific heat of the mixture is less than the calculated mean value.

(3) When the two components form an additive compound with

a development of heat, and the resulting system consists of an equilibrium mixture of the two pure components and the compound, the specific heat of the mixture is greater than the calculated mean value.

Schultze determined the specific heat of nitrobenzene at different temperatures, and found that it diminishes gradually from 0·3582 at 10° to 0·3286 at 65°, and then increases to 0·3939 at 120°. The higher value at the lower temperatures is caused by the absorption of heat energy in the splitting up of the complex molecules, and the later rise with rise in temperature is typical of the general behaviour of non-associated liquids. When nitrobenzene is mixed with benzene, the equilibrium between the single and double molecules of the former is shifted, because of the dilution effect, in favour of the single molecules; consequently, the specific heat of the nitrobenzene constituent of the mixture is lowered, and that of the other component, benzene, being unaltered, the difference between the specific heat of the mixture and the calculated mean is accounted for. In this way the abnormally low specific heats of all mixtures included in (2) are explained. In a similar manner, the abnormally high specific heats of mixtures described in (3) are attributed to the absorption of heat occasioned by the thermal decomposition of the compound with rise in temperature.

Dolezalek has propounded a theory of binary mixtures by means of which, from a knowledge of the partial pressures of the components in the vapour phase in equilibrium with the liquid phase of a binary mixture, it is possible to determine the constitution of the liquid mixture and the equilibrium between the simple and complex molecules or between an additive compound and its two components (*Zeitsch. physikal. Chem.*, 1908, **64**, 727).

Schultze, making use of the equilibrium constant determined by the above method, has shown that, if the double molecules in the case of a mixture containing an associated component, or the additive compound where the two components unite chemically, are taken into account, the specific heats of the mixtures can be calculated, and that the values thus deduced are in good agreement with those found by experiment.

It is evident, from the foregoing observations, that since the simple mixing of chemically indifferent, non-associated liquids is not accompanied by any thermal effect, the magnitude of any heat change resulting from the mixing of two liquids may be regarded as a measure of the extent of combination; or of molecular dissociation; or, as is more frequently the case, the combined effect of these two actions. Further, the difference between the calculated and observed specific heats may be regarded as a measure of

the extent to which dissociation of the compound or of the double molecules depends on rise in temperature.

A very extensive research on the heat developed when water is mixed with methyl, ethyl, and propyl alcohols, and on the specific heats of these mixtures, has been carried out by Bose and Müller (*Nachr. K. Ges. Wiss. Göttingen*, 1906, 278) and by E. and M. Bose (*ibid.*, 1906, 309), and it would appear that the results of this investigation, which was undertaken for another purpose altogether, might be used to test the validity of Denison's conclusions, derived from viscosity data, as to the compounds present in these mixtures (*Trans., Faraday Soc.*, 1912, **8**, 20). It is apparent, however, from Bose's results, that the molecular complexity of both components in these mixtures has such a disturbing influence on both the heat of mixing and the specific heats as to make such a comparison very difficult. Further, the comparatively small amount of heat developed when these substances are mixed does not tend to simplify the problem.

In such substances as acetone, pyridine, dimethylaniline, and quinoline, molecular association is very slight indeed, and in *o*-chlorophenol it is of a much lower order than in water and the alcohols; therefore, for mixtures of *o*-chlorophenol with any of the bases mentioned, this source of complication is very considerably reduced, and in addition, the amount of heat developed on mixing these substances is many times larger than that produced when alcohols are mixed with water. Taking these two factors together, it appeared probable that the determination of the heats of reaction of some of these substances and the specific heats of their mixtures might lead to valuable information regarding the constitution of their mixtures in the liquid state.

Experimental.

In deciding on a method for the determination of heats of reaction, it is necessary to consider the following points:

(1) The order of magnitude of the heat effect.

(2) The quantities of the materials available.

(3) The accuracy with which the specific heats of the reacting substances and their mixtures can be determined.

(4) The order of accuracy required.

In the ordinary apparatus for the determination of heats of reaction the two liquids are placed in separate vessels, their temperatures ascertained, and then one liquid is run into the other and the rise in temperature determined. The corrections that have to be applied in such a method involve heat changes by

conduction and radiation and a knowledge of the heat equivalents of various parts of the apparatus. Many of these are doubtful quantities, and in order to minimise their effect, comparatively large amounts of the reacting liquids are used, so that the heat equivalents of the various parts of the apparatus concerned constitute only a small fraction of the total heat capacity. It follows, therefore, that if this method be adopted, comparatively large quantities of the reacting substances are required.

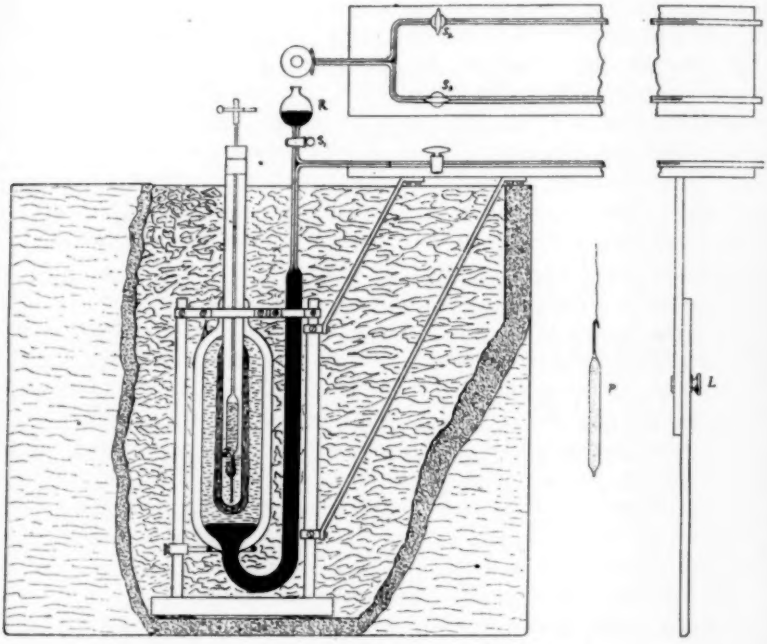
Further, since the accuracy with which the heat of reaction can be determined depends largely on the precision with which the specific heats of the reacting substances and their mixtures are known, the acquirement of these necessary data involves a large amount of careful experimental work. This is especially so when the reactions concerned are balanced ones and change in temperature causes a shift in the equilibrium, because the specific heats of such mixtures are usually very variable. On account of these difficulties and the cost of some of the substances rendering their employment in large quantities prohibitive, it was found necessary to adopt some method in which relatively small quantities of the substances are sufficient, and, if possible, a method by which the difficulties involved in the specific heats might be evaded.

We have, fortunately, in Bunsen's ice calorimeter, a method which can be used for this purpose; the question of specific heats can be eliminated altogether, and only small quantities of the substances need be employed. There remained, however, one question to decide. Would the amount of heat liberated when such volumes of the liquids as can be used in this instrument are mixed come within the limits of accurate measurement by this method? A few preliminary experiments were made to determine the magnitude of the heat change involved, and the results indicated that the ice calorimeter method would be suitable; consequently, an instrument of appropriate dimensions was designed.

The calorimeter itself was made by Müller, Orme and Co., and a diagrammatic picture of the instrument as it was set up for use is given in Fig. 1. The diameter of the inner tube was approximately 2 cm., and a length of about 17 cm. of it was in the bulb containing the water and mercury, and a similar length of the tube projected out of the bulb. A vacuum jacket enclosed the bulb and a short piece of the tube. A length of about 10 cm. of the upper part of the other limb of the instrument consisted of capillary tubing of 1 mm. bore, and terminated with a mercury reservoir, R, with the stop-cock, S_1. The object of having the upper part of this limb made of capillary tubing was to keep as small as possible the volume of mercury in the part of the tube

near the surface of the ice, where it is subject to slight temperature variations. Since the quantities of heat which had to be measured were likely to vary considerably, it was decided to fit the instrument with two side-tubes connected together, and to the vertical tube of the instrument just below the reservoir, as shown in the diagram. One of these tubes had a bore of about 1 mm. diameter, and the other was a capillary tube of approximately 0·17 mm. bore. Stop-cocks, S_2 and S_3, inserted in these tubes enable either of them to be used at will, the other being put out of action.

FIG. 1.



These tubes were supported over scales a metre long on a horizontal table, *T*, which was fixed at one end to the stand carrying the calorimeter and supported near the other end by an adjustable leg, *L*.

The calorimeter, fixed in its stand, was placed in the centre of a cylindrical tank of about 50 litres' capacity, which was filled with clean ice broken into small pieces. The tank itself was lagged with a thickness of about 10 cm. of cotton-wool and covered with felt. The great trouble with ice calorimeters is to reduce the heat change between the water inside the calorimeter and the

surroundings to such an extent as to ensure the "creep" of the mercury in the capillary tube being steady and sufficiently small, compared with the total movement during an experiment, as to make this, the only correction in which there is any uncertainty, a small one. The most effective way of doing this is to enclose the bulb of the calorimeter in a vacuum jacket, which very materially reduces the rate of exchange of heat. It was also found advisable to break up the ice required for the bath, and allow it to remain in contact with distilled water in an ice-chest some hours before it is used. This latter precaution is necessary because the temperature of the interior parts of large blocks of ice is generally below 0°. By adopting these precautions, the creep of the mercury in the smaller tube was reduced to about 2 mm. an hour, and to less than 0·5 mm. an hour in the larger tube.

The capillary tubes and scales were calibrated in the usual way, and tables constructed for each tube, so as to give the volume of the tube between the zero and any point on the scale. Readings were taken to the nearest 0·1 mm. by means of a small telescope supported on a stand which could be moved along the table between the two tubes. The contraction in volume equivalent to 1 calorie was determined by introducing a known weight of water at a known temperature in a pipette of the form indicated by *P* in the figure, and made from a thin glass test-tube. The pipette and contents were heated to 20·00°, and the mean specific heat of water between 0° and 20° was taken as 1·003. From the calibration tables the volume of the tube between the positions occupied by the meniscus of the mercury before the pipette was introduced and when it had become steady after its introduction was determined, due allowance having been made for the creep. A thermometer placed alongside the tube gave the temperature at which the change in volume was measured, and this, when reduced to 0°, gave the contraction in volume produced by a known quantity of heat.

Two experiments were made with each tube, and the results obtained were as follows:

(1)	Wide tube.	1 calorie	≡ 0·001133	c.c.	contraction.
(2)	,,	,,	0·001134	,,	,,
(3)	Narrow tube	,,	0·001132	,,	,,
(4)	,,	,,	0·001133	,,	,,
		Mean	= 0·001133	,,	,,

The method of procedure in determining the heat of reaction when two liquids are mixed together was as follows: A pipette which could be closed at the top by means of a piece of rubber tubing and a clip was filled with one of the liquids, and weighed.

The pipette, with its contents, was then placed in a dry test-tube surrounded with crushed ice and allowed to cool approximately to zero. It was then transferred quickly to the calorimeter, and its contents were run into the inner tube. The empty pipette was then withdrawn and weighed; in this way a known weight of one of the constituents was determined. For the second constituent a clean, dry pipette of the form shown in the diagram was fitted with a cork, rubber tube, and clip, and weighed. The liquid was then drawn in, and the greater part of the capillary at the end of the pipette emptied, any liquid adhering to the outside being wiped off. By weighing the pipette thus filled, the weight of the second constituent was determined. As before, this pipette with its contents was cooled down approximately to 0° and then introduced into the calorimeter tube. The diagram in Fig. 1 shows the arrangement at this stage; the first liquid is shown in the bottom of the tube, and the pipette containing the second liquid is shown with its narrow tip dipping into the former and reaching almost to the bottom of the calorimeter tube. The object of the circular bend in the small tube at the end of the pipette was to prevent any possible drainage of the liquid in the pipette down the walls of the narrow tube into the other liquid.

Having brought the mercury to a suitable position in the capillary tube, which was easily done by means of the mercury reservoir and stopcock, readings were taken at regular intervals. When the readings showed that the movement of the mercury in the capillary tube was steady and equal to the known creep, the clip was removed from the rubber tube on the end of the pipette, and the liquid in the latter forced out into the calorimeter tube, where it mixed with the other liquid. Complete mixing was easily effected by forcing a few bubbles of air through the mixture and rotating the pipette in the tube. In order to wash out all the liquid in the pipette, some of the mixture was drawn up into it and forced out again. Readings continued to be taken at regular intervals until the movement of the mercury was again quite steady; then, allowance having been made for the creep and the temperature of the capillary tube, the quantity of heat produced, in calories, was obtained from the expression:

$$\frac{\text{Change in volume at } 0^\circ}{0{\cdot}001133}$$

For the determination of the mean specific heats between 0° and 20°, pipettes of about 10 c.c. capacity were made from test-tubes by drawing out the ends to thin-walled capillaries. After almost filling the pipette with the mixture, one capillary was sealed off and the end of the other bent through two right angles. The

tube, with its contents, is shown in Fig. 1 at *P*. The amounts of liquid and glass in the tube were determined by weighing. The tube, with its contents, was heated to 20·00° in a thermostat near the calorimeter and transferred to the latter as rapidly as possible.

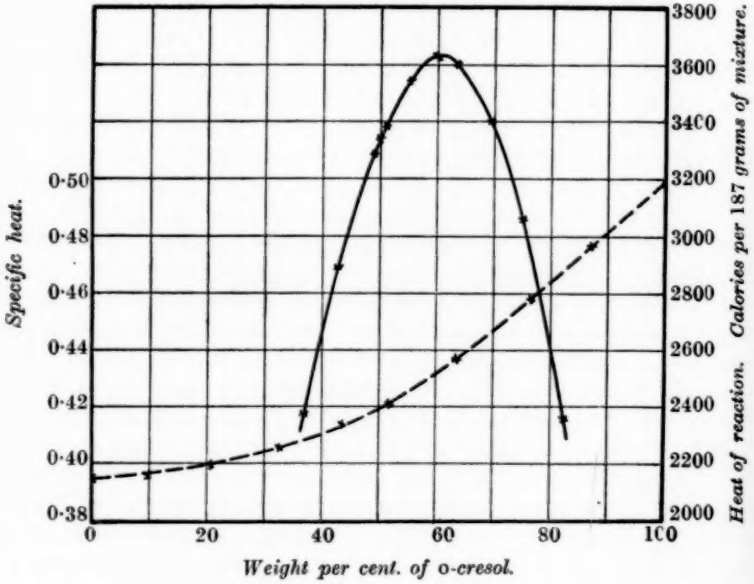
The mean specific heats between 0° and 100°, as well as those between 0° and 20°, were determined for mixtures of *o*-chlorophenol and pyridine. The heater used for this purpose consisted of a glass tube, 1·5 cm. in diameter and 35 cm. long, fixed, by means of corks at each end, in the centre of a slightly shorter glass tube 6 cm. in diameter. Steam was passed through the annular space between the two tubes, and the small tube containing the mixture was supported by means of fine thread in the middle of the inner tube of the heater, and the ends of the latter were closed by means of plugs of cotton-wool. The heater itself was set up in a vertical position at a short distance above the calorimeter, and in such a way that the inner tubes of the two instruments were co-axial. After the tube containing the mixture had been in the heater for a sufficiently long time, the latter was lowered until it almost touched the calorimeter; then the cotton-wool plugs were removed, and the small tube containing the mixture was shot out of the heater into the calorimeter as rapidly as possible. In this way there was little risk of cooling during the transference from the heater to the calorimeter. In order to test the accuracy of this method of determining heats of reaction, the heat of neutralisation of hydrochloric acid with sodium hydroxide in dilute solutions was determined. A solution of hydrochloric acid was made up, and adjusted so that it was accurately 0·25*N*. Sodium hydroxide solution free from carbonate was made exactly equivalent to the hydrochloric acid solution. The pipette used for these experiments was calibrated so as to be able to measure a known volume of the acid and alkali solutions, since these were made up by volume, and not by weight: 11·65 c.c. of each solution were employed, and the smaller capillary tube of the calorimeter was used to measure the amount of heat developed. The mercury meniscus receded for a length of about 35 cm. during this experiment; it will be seen, therefore, that quite an accurate measurement could be made so far as this part of the experiment is concerned. This experiment gave a result of 14,670 calories as the heat of neutralisation of 1 gram-molecule of hydrochloric acid with an equivalent amount of sodium hydroxide. A second experiment of a similar kind gave the result 14,690 calories. Thomsen's value for the heat of neutralisation of these two substances at the same dilution and at 0°, obtained by extrapolation from results obtained for different temperatures, is 14,677 calories.

Duplicate experiments were made to determine the order of accuracy with which the specific heats could be determined, and it was found that the extreme variation was not more than 3 or 4 parts per thousand. The specific heats may therefore be regarded as probably accurate within one unit in the third decimal place.

In the following tables the weights of the different substances used in the heat of reaction experiments are given, from which it will be seen that the total weight of the mixture was usually between 10 and 20 grams. The last column in the tables shows

FIG. 2.

o-Cresol and pyridine.



the amount of heat, in calories, which would be developed if the total weight of the reaction mixture were equal to the sum of the gram-molecular weights of the two components of the mixture.

o-Cresol and Pyridine.

The results obtained for mixtures of *o*-cresol and pyridine are given in tables I and I*a*, and are shown graphically in Fig. 2. The full-line curve is the heat of reaction curve, and the broken line one shows the mean specific heats between 0° and 20°.

TABLE I.

o-Cresol and Pyridine.

Weight of *o*-cresol in grams.	Weight of pyridine in grams.	Percentage of *o*-cresol.	Heat of reaction in calories per 187 grams of the mixture.
5·22	8·88	37·0	2374
6·44	8·77	42·35	2889
6·48	8·70	42·75	2893
8·45	8·74	49·15	3286
6·89	6·86	50·1	3341
9·10	8·61	51·3	3386
7·45	6·06	55·15	3547
9·11	6·12	59·8	3634
9·12	6·05	60·1	3624
9·11	5·20	63·6	3604
9·13	4·05	69·3	3407
8·86	2·96	74·95	3066
9·15	1·96	82·5	2365

TABLE I*a*.

o-Cresol and Pyridine.

Percentage of *o*-cresol.	Mean specific heat between 0° and 20°.	Percentage of *o*-cresol.	Mean specific heat between 0° and 20°.
0·00	0·395	51·9	0·421
9·55	0·396	63·6	0·437
20·65	0·400	76·5	0·458
32·68	0·406	87·2	0·477
43·80	0·414	100·0	0·499

m-*Cresol and Pyridine.*

Mixtures of these two substances were made up in the calorimeter, and the heat developed was measured as before. The mean specific heats between 0° and 20° were also determined. The experimental figures are given in tables II and II*a*, and are shown graphically in Fig. 3.

TABLE II.

m-*Cresol and Pyridine.*

Weight of *m*-cresol in grams.	Weight of pyridine in grams.	Percentage of *m*-cresol.	Heat of reaction in calories per 187 grams of the mixture.
2·40	11·65	17·1	957
5·42	11·65	31·75	1722
5·67	8·88	39·0	2124
7·40	8·79	45·75	2443
8·83	8·51	50·95	2634
6·54	4·77	57·8	2826
8·16	4·75	63·2	2847
8·56	4·25	66·9	2752
11·17	4·23	72·5	2571
8·67	2·09	80·5	2049
12·20	1·32	90·15	1163

FIG. 3.

m-Cresol and pyridine.

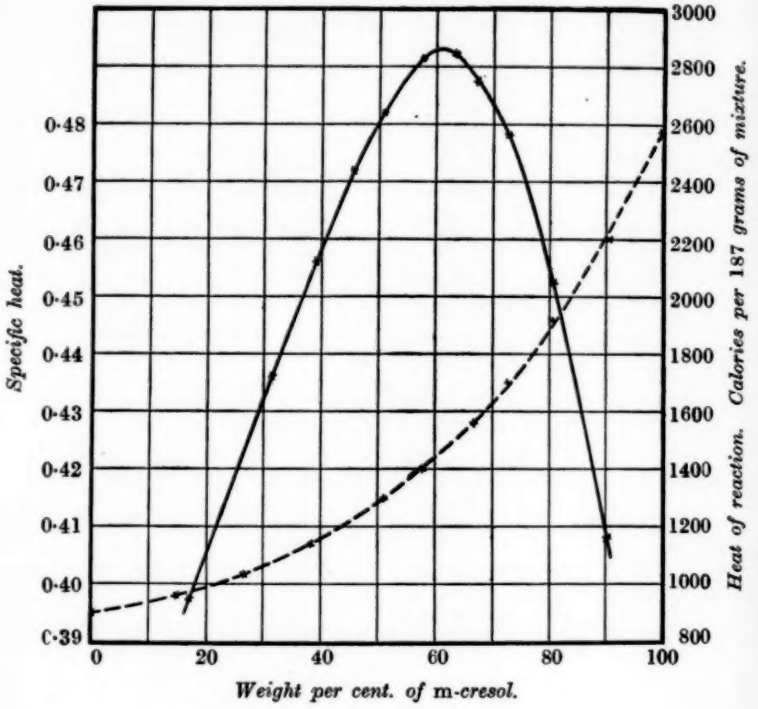


TABLE II*a*.

m-Cresol and Pyridine.

Percentage of *m*-cresol.	Mean specific heat between 0° and 20°.	Percentage of *m*-cresol.	Mean specific heat between 0° and 20°.
0·00	0·395	66·9	0·428
14·47	0·397	72·5	0·435
26·75	0·402	80·5	0·446
38·43	0·407	90·9	0·460
50·95	0·415	100·0	0·479
57·80	0·420		

o-Chlorophenol and Dimethylaniline.

The heats of reaction of these two substances and the mean specific heats between 0° and 20° of their mixtures were determined in the same way as before. Tables III and III*a* contain the experimental figures, and Fig. 4 shows the results graphically.

FIG. 4.

o-Chlorophenol and dimethylaniline.

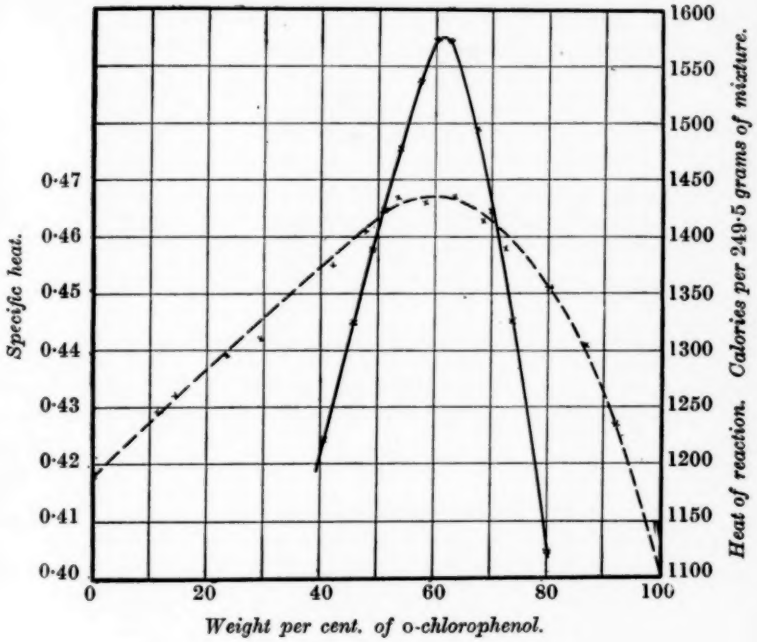


TABLE III.

o-Chlorophenol and Dimethylaniline.

Weight of *o*-chloro-phenol in grams.	Weight of dimethyl-aniline in grams.	Percentage of *o*-chloro-phenol.	Heat of reaction in calories per 249·5 grams of the mixture.
7·05	10·35	40·5	1223
7·04	8·36	45·7	1325
7·98	8·30	49·0	1389
8·72	8·32	51·2	1423
9·85	8·32	54·2	1479
9·79	7·26	57·4	1538
8·87	5·79	60·5	1574
10·03	5·99	62·6	1573
10·64	5·77	64·85	1543
10·63	5·17	67·25	1495
10·18	4·39	69·85	1423
10·88	3·89	73·65	1326
10·90	2·72	80·0	1123

TABLE III*a*.

o-Chlorophenol and Dimethylaniline.

Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.	Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.
0·00	0·418	58·4	0·466
11·30	0·429	63·75	0·467
14·55	0·432	68·3	0·463
23·45	0·439	72·2	0·458
29·6	0·442	80·0	0·451
42·15	0·455	86·8	0·441
47·75	0·461	92·0	0·427
53·3	0·467	100·0	0·401

o-Chlorophenol and Quinoline.

The experimental figures obtained for these two substances and their mixtures are given in tables IV and IV*a*, and shown graphically in Fig. 5.

FIG. 5.

o-Chlorophenol and quinoline.

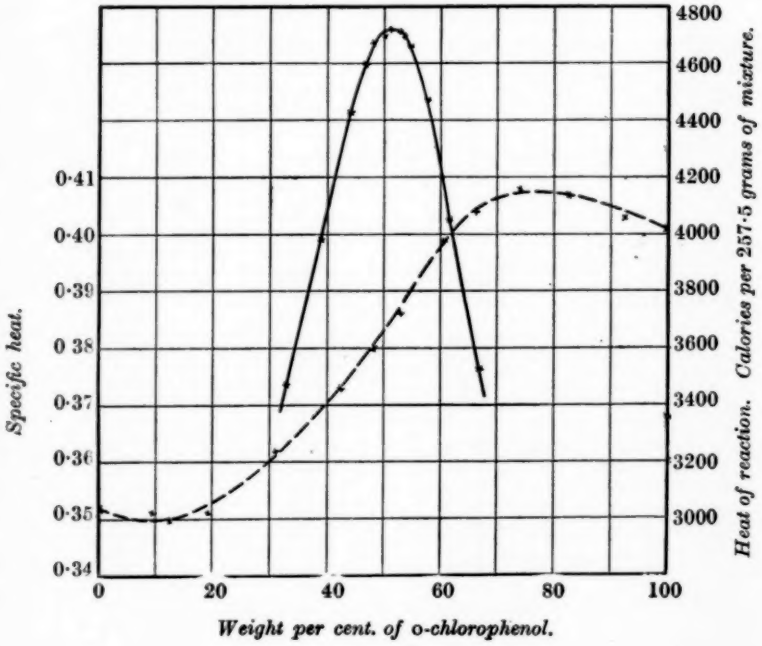


TABLE IV.

o-Chlorophenol and Quinoline.

Weight of *o*-chloro-phenol in grams.	Weight of of quinoline in grams.	Percentage of *o*-chloro-phenol.	Heat of reaction in calories per 257·5 grams of the mixture.
5·06	10·27	33·0	3476
6·02	9·50	38·8	3984
7·43	9·50	43·9	4429
8·50	9·68	46·75	4599
6·10	6·63	47·9	4681
6·66	6·64	50·1	4704
7·06	6·72	51·2	4726
10·13	9·46	51·7	4726
7·33	6·60	52·6	4715
10·50	9·10	53·6	4697
8·04	6·66	54·7	4663
7·98	6·60	54·75	4648
8·91	6·59	57·5	4475
10·44	6·57	61·4	4051
10·68	5·32	66·75	3528

TABLE IV*a*.

o-Chlorophenol and Quinoline.

Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.	Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.
0·00	0·352	53·0	0·386
9·38	0·351	60·5	0·399
12·37	0·350	66·1	0·404
19·19	0·351	73·95	0·408
31·10	0·362	82·55	0·407
42·50	0·373	92·3	0·403
48·25	0·380	100·0	0·401

Considerable difficulty was encountered in the determination of the heats of reaction of these two substances on account of the mixture freezing rather readily. No trouble of this kind was met with in the viscosity measurements, but when the two components were cooled to 0° before mixing, the agitation produced by the mixing frequently caused crystallisation to begin, which, of course, spoilt the experiment. The result obtained with the mixture containing 47·9 per cent. of *o*-chlorophenol had just started freezing when the experiment was finished, and may on that account be rather higher than it should be. All the other experiments recorded in the table were completed without the mixture freezing, although a number of others had to be abandoned because of this trouble.

o-Chlorophenol and Pyridine.

The results obtained for mixtures of these two substances are given in tables V and V*a*, and are shown graphically in Fig. 6. The mean specific heats of these mixtures were determined over two ranges of temperature: between 0° and 20° and between 0° and 100°. The lower of the two specific heat curves shown in the figure shows the results for the range 0° to 20°, and the upper curve shows those for the longer range.

FIG. 6.

o-Chlorophenol and pyridine.

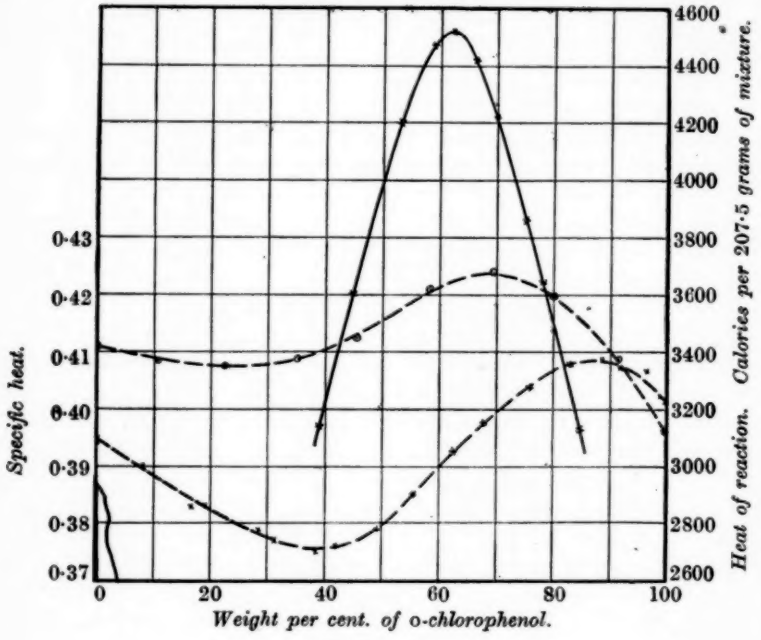


TABLE V.

o-Chlorophenol and Pyridine.

Weight of *o*-chloro-phenol in grams.	Weight of pyridine, in grams.	Percentage of *o*-chloro-phenol.	Heat of reaction in calories per 207·5 grams of the mixture.
5·30	8·30	39·0	3145
4·85	5·96	44·9	3607
4·75	4·20	53·1	4199
6·04	4·21	58·9	4472
6·83	4·20	61·9	4519
10·60	5·46	66·0	4421
9·63	4·12	70·0	4219
10·13	3·39	74·9	3867
12·96	3·67	78·0	3649
11·84	2·09	85·0	3134

TABLE V*a*.

o-Chlorophenol and Pyridine.

Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.	Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.	Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 100°.
0·00	0·395	55·3	0·385	0·00	0·411
8·23	0·390	62·45	0·393	10·63	0·409
16·75	0·383	67·75	0·397	22·50	0·408
19·11	0·383	76·0	0·404	35·15	0·409
28·70	0·379	83·0	0·408	46·4	0·413
31·25	0·377	88·5	0·409	58·5	0·421
38·50	0·375	91·6	0·407	69·8	0·424
42·0	0·376	96·5	0·407	79·9	0·420
49·3	0·379	100·0	0·401	91·6	0·409
—	—	—	—	100·0	0·396

o-Chlorophenol and Acetone.

Numerical details of the experiments made with these two substances and their mixtures are given in tables VI and VI*a*, and Fig. 7 shows these results graphically.

FIG. 7.

o-Chlorophenol and acetone.

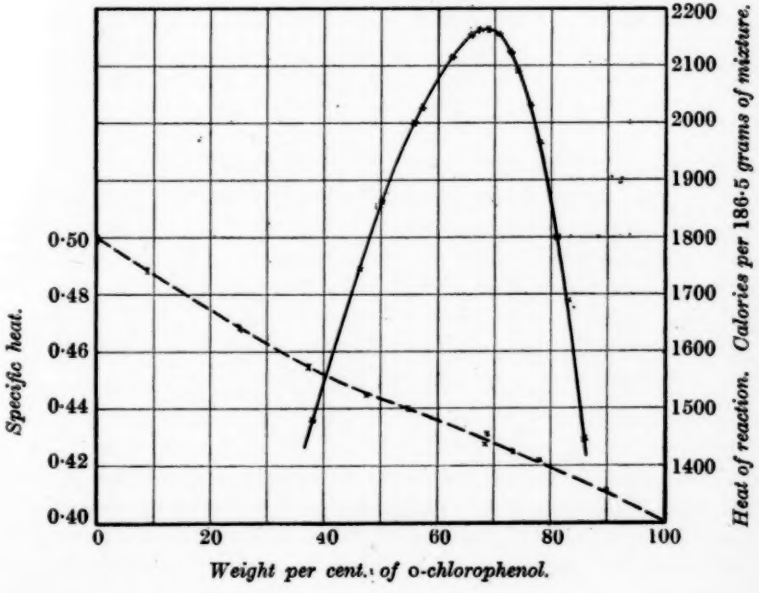


TABLE VI.

o-Chlorophenol and Acetone.

Weight of *o*-chloro-phenol in grams.	Weight of acetone in grams.	Percentage of *o*-chloro-phenol.	Heat of reaction in calories per 186·5 grams of mixture.
5·07	8·28	38·00	1480
6·05	6·94	46·55	1744
7·21	7·21	50·0	1863
9·15	7·21	55·95	2006
9·26	6·90	57·3	2025
10·59	6·39	62·4	2116
8·94	4·57	66·2	2152
8·93	4·04	68·85	2163
10·82	4·50	70·65	2157
9·48	3·62	72·45	2125
10·53	3·70	74·0	2092
10·86	3·42	76·3	2032
10·92	3·10	78·1	1967
10·08	2·38	80·9	1801
10·50	2·18	82·9	1689
11·06	1·78	86·1	1448

TABLE VI*a*.

o-Chlorophenol and Acetone.

Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.	Percentage of *o*-chloro-phenol.	Mean specific heat between 0° and 20°.
0·00	0·500	68·95	0·431
9·02	0·489	73·3	0·425
25·35	0·468	78·0	0·422
37·6	0·455	80·8	0·423
47·65	0·445	90·0	0·411
55·0	0·440	100·0	0·401
68·7	0·428		

o-Chlorophenol and Diphenylmethylamine.

One experiment was made on the heat of reaction between these two substances, and it was found to be negative. 10·80 Grams of *o*-chlorophenol and 9·16 grams of diphenylmethylamine were used, and the amount of heat absorbed by the mixture at 0° was 17·74 calories, which is equivalent to an absorption of 285 calories for 311·5 grams—the sum of the molecular weights in grams of these two substances—of a mixture of this composition.

Discussion of Results.

The large values of the heats of reaction of all the mixtures studied in the course of this investigation, with the exception of the one containing diphenylmethylamine, is ample evidence of the formation of compounds taking place to a considerable extent, and

these results may be regarded as a definite answer in the affirmative to the question as to whether the compounds are present in the liquid state of the mixture.

The heats of reaction for mixtures of pyridine and *o*-cresol are considerably greater than for the corresponding mixtures of pyridine and *m*-cresol. This, at first sight, seems rather strange, because a larger proportion of compound might be expected in the mixture containing the *m*-cresol, since this substance is more strongly acid than *o*-cresol. It does not follow, however, that combination between pyridine and *m*-cresol is less extensive than it is between pyridine and *o*-cresol. Association of the molecules in the liquid state is far more extensive in *m*-cresol than in *o*-cresol, and the splitting up of these molecular complexes, which must precede the formation of compounds with pyridine, will cause the absorption of a considerably larger amount of the heat resulting from the formation of compounds in the mixtures containing *m*-cresol than will be the case in the corresponding mixtures containing *o*-cresol; further, the heat of formation of the pyridine–*o*-cresol complex may be greater than that of the pyridine–*m*-cresol compound.

An interesting feature in the heat of reaction curves for both these mixtures is the position of the maximum points. In neither case is the maximum on the curve on the ordinate corresponding with 57·75 per cent. of cresol, the proportion of cresol in the equimolecular mixture.

The heat of reaction between such substances as are now under consideration should be regarded as the algebraic sum of the heat effects of three separate processes. These are:

(1) The dissociation of complex into simple molecules of the phenolic constituent.

(2) The dissociation of complex into simple molecules of the basic constituent.

(3) The formation of the compound molecules by the combination of the simple molecules of the two components.

The first two of these processes cause an absorption of heat, and the last produces a development of heat. Now a curve showing the heat of formation of the phenol-base compound could be constructed from the heat of reaction curve shown in the diagram by raising each point on the latter curve by an amount equal to the sum of the thermal effects of the dissociation of the complexes of the separate components if this were known. It is not easy, however, to determine this last-mentioned quantity, but in the mixtures of pyridine with *o*- and *m*-cresols, the latter constituent is certainly much more associated than pyridine, and if there is

any change in the amount of heat absorbed by dissociation processes in mixtures ranging from about 50 to 70 per cent. of cresol, it will probably increase with increasing content of cresol. It appears, therefore, that the maximum on the heat of formation curve would be at a point corresponding with the same or a very slightly higher concentration of cresol in the mixture as the maximum point on the heat of reaction curve. In any case, the amount of heat absorbed by dissociation processes in these mixtures, being very much smaller than the amount of heat evolved by the formation of the compound, cannot influence the position of the maximum point on these curves by more than a very slight amount.

Since these are the only processes involving heat changes, it follows that although the lengths of the ordinates of the heat of reaction curve cannot be regarded as a measure of the extent of the formation of compounds, the position of the maximum point on that curve may be taken as indicating, with a fair degree of certainty, the composition of the mixture which contains the maximum amount of compound. What, then, can be the cause of a difference of 3 per cent. in the content of cresol between the mixture which contains the maximum proportion of compound and the one which contains the two components in equimolecular proportions? The answer to this question is not very obvious, but the following points may have some influence, and are worthy of consideration:

(1) On account of the difference in density and in the molecular weights of the two components of a mixture, the total number of molecules in a certain volume will depend on the composition of the mixture, and since the amount of compound formed depends on the product of the concentrations of the reacting substances in the equilibrium mixture, the composition of the mixture in which a maximum of compound is formed will be influenced by the density and molecular weights of the two components; it will only occur in the 50 molecular per cent. mixture when the sum of the concentrations of the two components is independent of the composition of the mixture.

(2) In a reaction of the type represented by the equation:

$$A + B \rightleftharpoons AB,$$

the equilibrium constant depends on the concentrations of A, B, and AB in the equilibrium mixture, and if one of the components, A, for example, forms double molecules, there will be a second equilibrium:

$$2A \rightleftharpoons A_2,$$

and since the concentration of the AB molecules depends on the

concentration of A, and not A_2, it follows that the total concentration of the substance A—single and double molecules—must be greater than that of B in order to obtain equimolecular concentrations of A and B.

(3) The nature of the solvent is well known to influence the position of equilibrium in such reversible processes as esterification. In the binary mixtures under discussion, the liquid itself may be considered as its own solvent the properties of which, such as dielectric constant, etc., undergo continuous change as the composition of the mixture varies. This may influence the equilibrium constant.

The specific-heat curves for mixtures of pyridine with *o*- and *m*-cresols lie below the straight line representing the calculated means. Since the specific heat of a dissociating system is abnormally large, it follows that little dissociation of the pyridine–cresol complexes can take place as the temperature is raised from 0° to 20°, and the cause of the sag in these cases must be the result of thermal dissociation of complex cresol molecules.

The most remarkable feature about the heat of reaction curve for mixtures of *o*-chlorophenol and dimethylaniline, is the position of the maximum, which is situated at a point corresponding with a mixture containing 61·5 per cent. of *o*-chlorophenol, whereas the equimolecular proportion mixture contains but 51·5 per cent. of this component. In this case the number of molecules per unit volume of the mixture increases as the mixture becomes richer in *o*-chlorophenol. The factor considered in (2) probably plays an important part in fixing the equilibrium of this mixture. Dimethylaniline has a much lower dielectric constant than any of the other bases used in these experiments, a fact which might provide favourable conditions for the formation of A_2 molecules, which would mean that a correspondingly higher percentage of *o*-chlorophenol would be necessary to bring up the concentration of single molecules of A for a maximum proportion of compound to be formed.

The specific heat curve for this mixture is typical of that of a dissociating system. It is noteworthy that the maximum deviation on the specific heat curve from the straight line representing calculated means occurs at approximately the same position as the maximum on the heat of reaction curve. There is strong evidence that the mixture which contains the maximum proportion of compound is the one containing 61·5 per cent. of *o*-chlorophenol.

Mixtures of *o*-chlorophenol and quinoline give a maximum on the heat of reaction curve at 51·5 per cent. of *o*-chlorophenol. This is 1·5 per cent more than is required by equimolecular propor-

tions. The sinuous nature of the specific heat curve for mixtures of these two substances suggests that with mixtures rich in *o*-chlorophenol, thermal dissociation of the compound takes place with rise in temperature much more readily than with mixtures rich in quinoline.

The composition of the mixture which gives the maximum amount of heat of reaction in the case of *o*-chlorophenol and pyridine contains 61 per cent. of the former; the equimolecular mixture requires 62 per cent. of this compound. The large sag in the specific heat curve for mixtures of these two substances is remarkable. The cause of this cannot be association of the pyridine molecules, since this is known to be very slight indeed, if it exists at all. Mention has previously been made of the dissociating power of pyridine and its fairly high dielectric constant. These factors may be responsible for the low specific heats between 0° and 20° of mixtures rich in pyridine.

Since the dielectric constant falls with rise in temperature, the dissociating power of the liquid, which depends to some extent on its dielectric constant, must also diminish with rise in temperature. Further, the dissociation constant increases with rise in temperature, and if this may be taken as a measure of the combining power, it follows that, so far as these factors are concerned, rise in temperature should promote the formation of compounds. An opposing factor is the thermal dissociation brought into play by rising temperature. The shift in the equilibrium depends on the joint effect of these three factors. It is evident that in this case, between the temperatures 0° and 20°, the dissociating factor is overpowered by the others which promote compound formation. With mixtures of *o*-chlorophenol and dimethylaniline the third dissociating factor is predominant.

The specific heat curve for mixture of *o*-chlorophenol and pyridine for the range 0° to 100° shows that the effect of thermal dissociation becomes more and more influential as the temperature rises, and it is obvious that a curve showing the mean specific heats for a range of, say, 50° to 100°, would be of the same form as that obtained for the *o*-chlorophenol and dimethylaniline mixtures.

The maximum on the heat of reaction curve for mixtures of *o*-chlorophenol and acetone occurs with the equimolecular proportion mixture, and the specific heat curve is almost a straight line, indicating that there is little change in the constitution of the mixture as the temperature is raised from 0° to 20°.

So far as the heat of reaction is concerned, only one compound is indicated in any of the mixtures examined, and in all cases it is the equimolecular compound. If any other compound is formed,

such, for example, as the one suggested by the viscosity curve at 0°, for mixtures of pyridine and *o*-chlorophenol, it must be of a far lower order of stability, since the energy change attending its formation is immeasurably small compared with that of the formation of the equimolecular compound.

In the equilibrium represented by the equation:

$$A + B \rightleftarrows AB,$$

if a and b represent the number of gram-molecules of A and B respectively that are used in making up the mixture, and if the equilibrium mixture contains x gram-molecules of AB, the equilibrium constant K will be given by the expression:

$$K = \frac{(a-x)(b-x)}{Vx},$$

where V is the total volume of the mixture. Now if the amount of compound formed were proportional to the heat of reaction, then x could be put equal to cH, where H is the heat of reaction and c is a constant. By making two mixtures containing different proportions of the reacting constituents and measuring the heat of reaction in each case, the following relations might be obtained:

$$K = \frac{(a_1 - cH_1)(b_1 - cH_1)}{V_1 cH_1}$$

$$\text{and } K = \frac{(a_2 - cH_2)(b_2 - cH_2)}{V_2 cH_2},$$

and since these two equations contain two unknown quantities only, they may be solved and the equilibrium constant determined.

On trying this with several results obtained with mixtures of *o*-chlorophenol and quinoline, it was found that c varied from 0·00020 to 0·00017 with a corresponding variation in K, so that it is evident that absorption of heat caused by the dissociation of the complex molecules interferes too seriously to allow of this method being used to obtain a trustworthy value of K.

The mean value of c from several determinations for mixtures of these two substances was 0·000185, and the corresponding value of K was 0·09. When the two components are in equimolecular proportions these constants indicate that 13 per cent. of the mixture consists of free quinoline and *o*-chlorophenol, 87 per cent. being combined, but this is necessarily only a very rough approximation.

In conclusion, I wish to acknowledge my indebtedness to Professor Philip for the use of apparatus and materials, and the kind interest he has taken throughout this work.

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XXXIX.—*A New Form of Distilling Flask, together with a Note on Benzyl Benzoate.*

By The Earl of Berkeley.

During the preparation of a somewhat large quantity of benzyl benzoate (b. p. 322°) two difficulties were encountered; these, which are inherent in the distillation of substances of high boiling point, are: first, as at the present time soft glass flasks only are obtainable, breakages were somewhat frequent, and secondly, on account of lagging troubles I could deal only with small quantities of liquid at a time, being forced to use 300 c.c. flasks.

A quartz flask obviates the first difficulty, but it is still subject to the second.

The following experiments were made to get a rough idea as to the effect of lagging.

A 300 c.c. quartz flask, having a neck 21 cm. long of about 2½ cm. diameter was covered by two thicknesses of asbestos cloth, and benzyl benzoate was distilled over at a constant rate of 10 c.c. in eighty seconds. Without altering the supply of gas or moving the burner (the bottom of the flask being fitted into a copper hemisphere), the asbestos round the neck was removed, and when the new constant rate of distillation was attained it was measured. The removal of the lagging was found to have almost exactly doubled the time required for the transference of 10 c.c. Replacing the benzoate by water and distilling at a constant rate of 10 c.c. in two hundred and ten seconds the experiment was repeated, with the result that there was very little difference in the rates; if anything, the water passed over somewhat faster after the removal of the lagging. At first sight this savours of a paradox, but Porter has shown (*Phil. Mag.*, 1910, [vi], **20**, 520) that for small brass tubes of ½ cm. diameter any lagging under 1 cm. thick increases the loss of heat. It is thus possible that for the materials used, the coating was not thick enough. Be this as it may, it is obvious that for liquids having high boiling points, lagging is necessary.

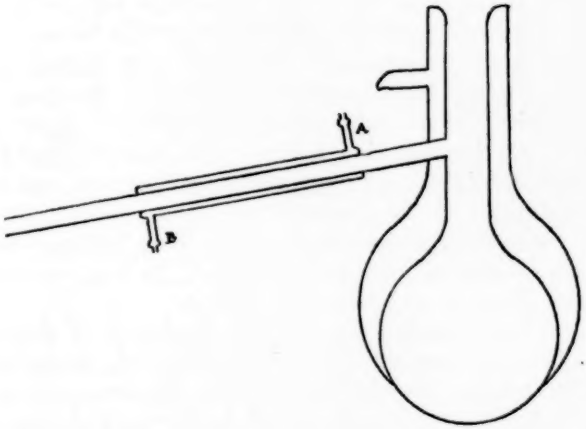
The ideal lagging is a vacuum jacket fused round the upper part of the flask, and in view of the advantage gained by even a partial vacuum (see below) it would seem worth attempting to make this of hard glass. As, however, no suitable glass is now available, the Silica Syndicate made me the 500 c.c. quartz vacuum jacketed flask shown in the figure.

The diagram needs no description, but it may be mentioned that

the tubulure *A* should be as close as possible to the end of the condenser (in quartz this is easily done) so that air given off when the water is heated by the condensing vapour will be carried away at once. *B* also should be near the end, to facilitate draining out the condenser. With the condenser close to the neck the side-tube can be washed out both quickly and with little loss of liquid.

Although the vacuum is not comparable to that of a Dewar vessel, yet with the new form of lagging I can distil, for the same consumption of gas, twice the quantity of the benzoate as I had previously obtained from an asbestos-lagged 300 c.c. flask.*

It may be noted that with the new flask the boiling liquid is visible, and I have observed an effect which is new to me. Hitherto distillation has been stopped immediately the temperature begins



to rise above the boiling point of the benzoate, and this takes place when but a small amount of liquid is left in the flask. I now find that before this stage is reached the whole space becomes filled—sometimes quite suddenly—with a thick cloud of liquid particles. Obviously the distillation should at once be stopped.

In this connexion, I would mention that, in the ordinary laboratory copper still, water particles can be prevented from passing over with the vapour by filling the still-head with a handful of asbestos-wool held in place by copper gauze. Projections fused into the neck of a quartz flask would enable a similar device to be tried for the benzyl benzoate; this I hope to do in the near future.

I am informed that gas given off by silica (when strongly heated)

* It is possible that better results would be obtained if the jacket were merely filled with magnesia.

makes it hard to obtain a high vacuum *; the gas, of course, may be dissolved in the quartz, in which case the difficulties are almost insuperable. I suspect, however, that the two main causes of the trouble are that when the material softens sufficiently, gas bubbles, which are generally to be found enclosed in it, burst and give up their contents; also, as is well known, a certain amount of gas passes through at red heat. These two difficuities might be overcome by first of all carefully selecting a quartz tube free from bubbles for the side-tube which is to be closed, and then arranging that it can be caused to fall in when there is a vacuum on both sides of it. This I apprehend could be done by means of a heating coil (say, of tungsten wire) placed round the tube.

It seems possible that if a charcoal vacuum could be obtained in the jacket of a suitably designed quartz flask, increased accuracy in the determination of high boiling points would result, and the apparatus would be specially valuable where it is desired to recover the liquid under observation; whilst for low boiling points an inverted soft glass Dewar vessel (containing a suspended thermometer and with the side-tube passing through both walls) joined to the top of the fractionating column by a mercury-sealed ground-joint would certainly avoid apparent changes of temperature due to liquid condensing on the thermometer.

These various suggestions are here outlined because the present shortness of labour leaves no prospect of getting the work done either with glass or with silica.

Note on the Preparation of Benzyl Benzoate.—I find that the yield in Claisen's method (*Ber.*, 1887, **20**, 646), namely, treating benzaldehyde with benzyl alcohol which has been converted into sodium benzoxide, may be improved considerably if care is taken that both the aldehyde and the alcohol are dry and freshly distilled. Under these conditions, twenty-four hours on a water-bath, the temperature of which should be as near as possible to 100°, will suffice (Claisen says heat for several days), and, further, the product is almost free from the aldehyde.

The following is an example from the laboratory note-book: 2·3 grams of sodium were dissolved in 30 c.c. of the alcohol; while the resulting sodium benzoxide was still nearly boiling, it was gradually added to 300 c.c. of freshly redistilled aldehyde. At the end of twenty-four hours on the water-bath the product was treated

* A really good vacuum would necessitate a slight modification in the flask, either the cork carrying the thermometer would have to be removed to a position outside the jacket where it would not be heated to the boiling point of the liquid, and could not therefore contribute impurities to the vapour; or a ground quartz stopper from which to hang a small thermometer would be required.

as detailed by Claisen, and then distilled, with the result that about 230 c.c. of benzyl benzoate were obtained, together with 50 c.c. of a mixture passing over between 308° and 320°; from the latter some 35 c.c. of pure benzyl benzoate were secured by crystallisation; no smell of the aldehyde could be detected in any of the fractions.

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XL.—*The Ignition of Mixtures of Methane and Air and Hydrogen and Air by Means of the Impulsive Electric Discharge.*

By SOSALE GARALAPURY SASTRY.

WITHIN recent years the subject of the electrical ignition of gases has received attention from W. M. Thornton, who has published a number of papers dealing with its different aspects (*Proc. Roy. Soc.*, 1914, **90**, 272; **91**, 17; 1915, **92**, 9). The variable factors of Thornton's investigations were: the nature and percentage of the inflammable gas or vapour; the pressure of the gaseous mixture; and the character of the electrical means of ignition. Under the last-named head were ignition by break-flashes, for which the voltage, current, and self-induction of continuous current, and the voltage, current, frequency, and self-induction of alternating current were varied; ignition by condenser discharge sparks, for which the capacity was varied; and ignition by the impulsive electric discharge from the secondary circuit of an induction coil, for which the current in the primary circuit was varied. Further, the material and surface of the poles were varied.

It will be seen that the subject, taking alone into consideration the number of factors involved, is a complicated one. The results obtained by Thornton seem to complicate the subject further, and to indicate that there is some factor other than those enumerated above which requires to be taken into account. For example, Thornton found (*loc. cit.*, p. 19) that the material of the poles had a profound influence on the ease of ignition of a mixture of coal-gas and air by the impulsive electric discharge, ignition being easiest when nickel poles were used, iron, aluminium, platinum, and copper following in the order named. With condenser discharge sparks, on the other hand, the order of metals for ease of ignition was copper, iron, nickel, aluminium, and platinum. There seems to be no adequate reason for this curious interchange

of positions of the metals required to give greatest ease of ignition when used as poles, for condenser discharge sparks and the impulsive electric discharge do not differ materially in character.

It is not the intention of the present author, however, to discuss the many anomalous results that have been obtained in the course of investigations of this character, but rather to examine one peculiar feature of Thornton's experiments which seemed to require a new theory as to the nature of ignition phenomena, namely, his so-called "stepped ignition."

Briefly, stepped ignition is characterised by sudden changes in the amount of energy required to cause ignition of a given inflammable gas when mixed with air as its percentage is increased from the lower to the upper limit. "In other words, it is claimed that continuous alteration of the proportions of gas and air in an explosive mixture is, or may be, accompanied by discontinuous alterations in the spark energy required for ignition" (Bone, "Presidential Address to the Chemical Section, British Association, Manchester," 1915). Stepped ignition occurs, according to Thornton's published data, with propane, ethane, methane, carbon monoxide, hydrogen sulphide, and hydrogen (and apparently does not occur with butane), when ignition is effected by condenser discharge sparks between platinum poles. The author has attempted to check this important discovery in the case of mixtures of methane and air and hydrogen and air, the former gas being chosen because of its connexion with explosions in coal mines, the latter because, according to Thornton, it exhibited four well-defined "steps" or stages of increased difficulty of ignition. In neither case has the author been able to obtain any indication of departure from a normal smooth type of curve, provided that care was taken that the experimental conditions throughout the determinations were maintained unaltered. The precautions necessary are described in the experimental portion of this paper.

Experimental.

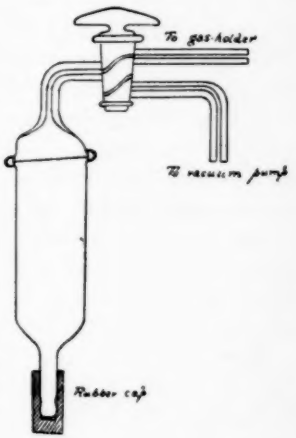
The apparatus consisted essentially of a glass explosion-vessel of about 50 c.c. capacity, with platinum electrodes sealed in, with which connexion could be established through a three-way tap with either a vacuum pump or a gas-holder containing the explosive mixture to be examined (see Fig. 1).

Ignition was effected by the impulsive electric discharge, that is to say, by single disruptive discharges from the secondary circuit of an induction coil the primary circuit of which was broken quickly by an automatic switch, the trembler being locked. The

measure of the ignitability of a given mixture was the magnitude of the current that had to be broken in the primary circuit to give at the spark-gap in the explosion-vessel a secondary discharge capable of igniting the mixture.

The method of experiment was as follows. The explosion-vessel was exhausted of air and filled at atmospheric temperature and pressure with some of the mixture contained in a two-litre gas-holder. A current of arbitrary value was passed through the primary of the induction coil, and fifty sparks (disruptive discharge) were then passed across the spark-gap in slow succession. If no ignition occurred, a slightly higher current was employed in the primary circuit, a fresh charge of the mixture being used, and so on, until a current was obtained at which ignition occurred invariably within the first few sparks. This minimum igniting current was checked for each mixture a dozen times or more, repeated trials being made also with currents slightly less than that at which ignition invariably occurred.

FIG 1.



Thus a whole range of mixtures of methane and air and hydrogen and air was obtained between the lower and upper limits of inflammability, the relative minimum igniting currents being expressed as currents in the primary of the particular induction coil used which, when broken in the same manner and at the same rate, gave across a fixed spark-gap a secondary discharge capable of igniting the mixture in the explosion-vessel. The results have no absolute value as measures of the energy required to cause the ignition of different mixtures, since the relation between the primary and the secondary circuits of the system was indeterminate; but if the intensity of the secondary discharge be regarded as proportional to the current broken in the primary circuit (an assumption the truth of which there is no reason to doubt), the "igniting currents" recorded express the relative energies required for the ignition of different mixtures.

In carrying out these experiments, it was found essential that there should be no modification whatsoever of two of the experimental conditions, namely, the rate of break of the primary circuit of the induction coil and the condition of the secondary spark-gap.

In preliminary experiments the primary circuit was broken by

hand by means of a quick-acting tumbler switch, but it was found that appreciable differences in the rate of break could be obtained by different experimenters. An automatic make and break for the primary circuit was therefore arranged. This consisted of a steel rod, which was brought into contact with a strong spring of strip steel by a slowly revolving turn-table, thus establishing electrical connexion through the primary circuit; the continued revolution of the turn-table forced the rod past the steel strip, which in springing back to its original position caused a quick break of circuit.

The condition of the spark-gap required particularly careful attention. Its magnitude had to remain unaltered throughout a series of experiments, for the greater the spark-gap the greater the igniting power of the secondary discharge. The spark-gap during all the experiments with mixtures of methane and air was 0·5 mm., whilst with the mixtures of hydrogen and air it was 0·25 mm.* It was essential that no trace of dust or dirt should attach to the platinum points forming the gap, or the passage of the discharge was impeded. It was found on several occasions that a mixture of which the "igniting current" was, say, 1·0 ampere, suddenly did not ignite at less than, say, 1·5 amperes. Such occurrences were always traceable to change in the condition of the platinum electrodes, for on cleaning the explosion-vessel by treatment with chromic and sulphuric acids the "igniting current" reverted to its original value. To avoid all possibility of error from such a cause, the plan was adopted of testing a "standard" mixture between each determination. The standard mixture of methane and air contained 8 per cent. of methane and had an "igniting current" of 1·30 amperes. A mixture containing, say, 7 per cent. of methane was tested, and the value 1·50 amperes finally determined as the minimum igniting current required for that mixture. The 8 per cent. mixture was then tested again; if the igniting current was still 1·30 amperes, the value 1·5 amperes for the 7 per cent: mixture was regarded as correct; if, as sometimes happened, the igniting current for the "standard" 8·0 per cent. mixture was found to be greater than 1·30 amperes, the explosion-vessel was cleaned with chromic and sulphuric acids, the "standard" tested again (it always reverted to its original value), and the previous mixture also re-tested.

The mixtures were prepared in glass gas-holders over glycerol and water, and were analysed before use, a check analysis being

* It was found necessary to use a smaller spark-gap for the experiments with mixtures of hydrogen and air, because with a gap of 0·5 mm. the least spark that could pass the gap could ignite the most sensitive mixture.

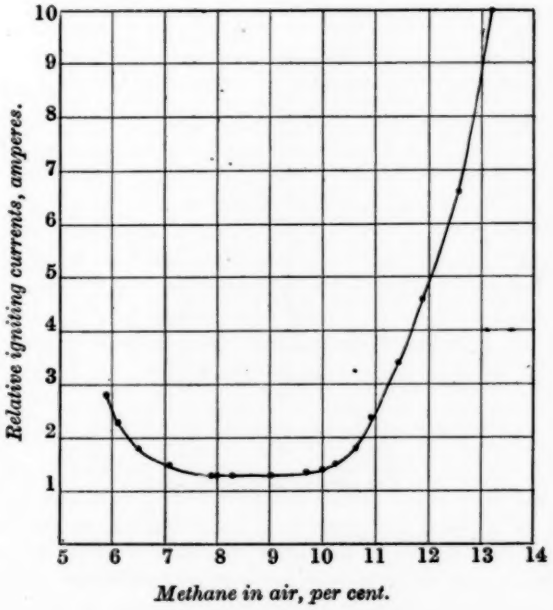
made at the end of each series of determinations with a particular mixture.

Results of Experiments.

(1) *Mixtures of Methane and Air.*—Spark-gap, 0·5 mm. The following table gives the relative igniting currents for all the mixtures tried. These figures are shown plotted as a curve in Fig. 2.

Methane in air, per cent.	Relative igniting current, amperes.	Methane in air, per cent.	Relative igniting current, amperes.
5·90	2·80	10·00	1·40
6·10	2·30	10·25	1·50
6·50	1·80	10·65	1·80
7·10	1·50	10·90	2·40
7·90	1·30	11·45	3·40
8·00	1·30	11·90	4·60
8·30	1·30	12·60	6·60
9·05	1·30	13·20	10·00
9·70	1·35		

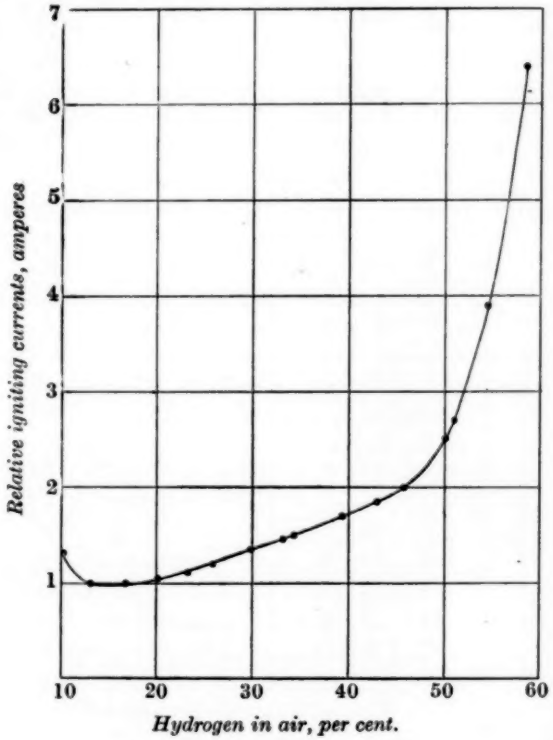
FIG. 2.



(2) *Mixtures of Hydrogen and Air.*—Spark-gap, 0·25 mm. The following table gives the relative igniting currents. These cannot be compared with the igniting currents for the mixtures of methane and air, since the spark-gaps were different.

Hydrogen in air, per cent.	Relative igniting current, amperes.	Hydrogen in air, per cent.	Relative igniting current, amperes.
9·75	1·50	34·35	1·50
10·15	1·30	39·30	1·70
13·10	1·00	42·95	1·85
16·75	1·00	45·80	2·00
20·30	1·05	50·00	2·50
23·20	1·10	51·15	2·70
25·80	1·20	54·45	4·40
29·80	1·35	58·65	6·40
33·10	1·45		

FIG. 3



Neither in the case of mixtures of methane and air nor in that of mixtures of hydrogen and air was any attempt made to determine the dilution limits of inflammability, the explosion-vessel not being of sufficient size to enable judgment to be formed as to whether flame could travel indefinitely. In the case of methane, the limits for downward propagation of flame (such as took place in the explosion-vessel used for these experiments) have been stated by Burgess and Wheeler (T., 1914, **105**, 2593) to be 6·0 per cent.

(lower) and 13·4 per cent. (upper). Mixtures containing less than 6·0 per cent. or more than 13·4 per cent. of methane could be ignited, and flame could travel a short distance, but such mixtures are incapable of indefinite propagation of flame downward.

The experiments described in this paper were carried out at the Home Office Experimental Station, under the direction of Dr. R. V. Wheeler. A portion of the work on the ignition of mixtures of methane and air was carried out in conjunction with Mr. C. Godfrey, to whom my thanks are due. I also wish to express my thanks to Mr. T. Mason, of the Home Office Experimental Station, for preparing and analysing the gas mixtures.

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London. [*Received, February 11th*, 1916.]

XLI.—*An Oxidation Product of Gallic Acid.*

By Hanns Bleuler and Arthur George Perkin.

This work originated from the desire to determine if it was possible to prepare cœruleo-ellagic acid (dihydroxyellagic acid) (T., 1911, **99**, 1442) by the direct oxidation of gallic acid. Cœruleo-ellagic acid can be readily obtained in this manner from ellagic acid, whereas it has long been known that ellagic acid is produced to some extent by the interaction of gallic and arsenic acids. This compound possesses much stronger dyeing properties than the lower hydroxylated members of the ellagic acid series, and would, no doubt, find technical employment could it be prepared in a more economical manner. No attention appears to have been devoted to the action of oxidising agents on gallic acid dissolved in sulphuric acid at temperatures from 100° upwards, and this may have arisen from the fear of the formation at first of rufigallic acid, which is itself more or less immune when submitted to this treatment.

Oxidation in the Presence of Concentrated Sulphuric Acid.

To a solution of 1·5 parts of arsenic acid in 16 parts of 96 per cent. sulphuric acid at 110°, 1 part of gallic acid was added and the mixture heated in an oil-bath to 120° for six hours. The brown-coloured liquid was poured into much water, the precipitate

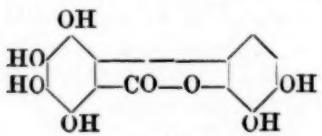
washed by decantation, collected, and dried at 160°. The finely powdered product was now digested with 5 parts of boiling acetic anhydride and a trace of pyridine for two and a-half hours, and the crystalline deposit (*A*) removed. By recrystallisation from much acetic anhydride this was obtained colourless, but was evidently a mixture, as its melting point, 290—305°, indicated. Further crystallisation being ineffectual, it was hydrolysed with sulphuric acid in boiling acetic acid, and after three hours the grey, crystalline powder was collected and converted into the benzoyl compound, employing benzoic anhydride (5 parts) with a little pyridine at 210—230°. On gradual cooling the solution commenced to deposit crystals, and at about 120° these were collected on a heated funnel and washed, first with a concentrated solution of benzoic anhydride in alcohol, and finally with alcohol. By recrystallisation from benzoic anhydride, colourless needles were obtained, which melted fairly sharply at 340°.

Found: C = 70·51; H = 3·04.

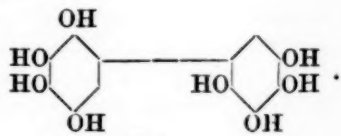
$C_{56}H_{30}O_{16}$ requires C = 70·17; H = 3·13 per cent.

The benzoyl compound when hydrolysed by long boiling with sulphuric acid, 8 parts, and acetic acid, 25 parts, yielded the colouring matter as a crystalline powder, which by means of the deep blue coloration it produced with dilute alkali and the melting point of its acetyl derivative was found to consist, without doubt, of cœruleo-ellagic acid.

The acetic anhydride mother liquors from (*A*) on partial concentration gave a further amount of acetyl derivative, melting indefinitely at about 290°. As it appeared likely that this consisted of a mixture of acetylcœruleo-ellagic and acetylflavellagic acids, its behaviour with boiling potassium hydroxide solution was studied for, in this manner, whereas flavellagic acid gives the 2:2′-lactone of 3:4:5:6:2′:3′:4′-heptahydroxydiphenyl-2-carboxylic acid (I), which is insoluble in water, cœruleo-ellagic acid yields only the readily soluble octahydroxydiphenyl (II):



(I.)



(II.)

The substance was digested with 5 parts of boiling 50 per cent. potassium hydroxide solution for a few minutes, and after dilution with water the liquid was immediately neutralised. The colourless needles, which separated on keeping, were soluble in dilute alkali with a bluish-violet coloration, and yielded an acetyl derivative

which melted at 232—234°. It evidently consisted of the compound (I), and this affords proof that the product from which it was derived contained acetylflavellagic acid.

The acetic anhydride mother liquor when again concentrated yielded after several days a small amount of an indefinitely crystalline deposit. By fractional crystallisation from acetic anhydride and by means of the benzoyl derivative, a bright yellow, crystalline compound was eventually isolated, which gave a crystalline sulphate, and is described in detail under the name of flavogallol in the second section of this paper.

The yield of mixed colouring matters obtained in this manner from gallic acid was unfortunately poor, the maximum (27·5 per cent.) being that obtained by heating the mixture to 110—120° for six hours, whereas the minimum (8 per cent.) was given at 100—110°.

*Oxidation in the Presence of Dilute Sulphuric Acid.**

In this connexion very many experiments were carried out, involving variations in the temperature, the time, dilution of the acid, and quantity of oxidising agent. As a result the following process appears to give the best result.

One and a-half parts of arsenic acid were dissolved in 2·5 parts of water, 16·5 parts of 96 per cent. sulphuric acid added, and the mixture was heated in an oil-bath to 110—115°. One part of gallic acid was now slowly added, causing the temperature to rise to 120°, at which it was maintained for six hours. The solution, which was at first of a reddish-brown colour, soon darkened, and effervescence occurred. The product was poured into twenty times its volume of water, the mixture allowed to remain overnight, and the resulting dull yellowish-green deposit washed by decantation and dried on the steam-bath. It was obtained in this way as a brownish-black, amorphous mass, the weight of which on the average was equivalent to 62 per cent. of the gallic acid employed. In the paste form it readily dyes mordanted fabrics, and, employing woollen cloth, the following shades are produced:

Chromium.	Copper.	Tin.	Iron.
Dull olive-yellow.	Pale brown.	Pale orange-yellow.	Brownish-black

These are of the type of those given by alizarine-yellow-*A* (trihydroxybenzophenone), and quite distinct from those yielded by flavellagic or cœruleo-ellagic acids. The isolation of the main constituent of this product in a pure condition was difficult, and in the earlier experiments a preliminary treatment with warm sodium

* A provisional patent for these processes has been secured.

hydrogen carbonate solution was employed. A yellow, amorphous sodium salt thus separates, which by filtration can be freed from the brownish-black liquid simultaneously produced, and when neutralised gives a dull yellow powder. Eventually, however, an acetylation process was adopted. The crude product (dried at 160°) was heated with 3 parts of acetic anhydride, and when the first violent reaction had subsided a trace of pyridine was added and the digestion continued for three hours. After remaining overnight, the crystalline deposit was collected, redissolved in 5·5 parts of boiling acetic anhydride, and allowed to remain for several hours without disturbance. A fine red powder thus separated in small amount, and this was rapidly collected, as the clear liquid on agitation soon commenced to deposit crystals. The residue was again treated in a similar manner with acetic anhydride, the trace of red substance which separated removed,* and the crystalline deposit, produced on evaporating the filtrate purified by recrystallisation from nitrobenzene. (Found, C=56·25; H=3·31, $C_{14}H_2O_8(C_2H_3O)_4$ requires C=56·17; H=2·98 per cent.) It consisted of needles melting at 343°, and was found to consist of acetylellagic acid.

The filtrate (*A*), after keeping for some hours, had deposited some quantity of cream-coloured crystals, and by evaporating the mother liquor fractionally, further amounts of a similar product could be isolated. The final dark-coloured, viscid liquid contained a considerable amount of an amorphous substance, and from this no definite compound was obtained.

By recrystallisation from acetic anhydride the fractions of acetyl compound could be obtained apparently pure, but the melting points varied from 240° to about 260°, and these were far from sharp. A benzoyl compound, however, of definite melting point could be isolated either from the hydrolysed acetyl compound or from the acetyl compound itself. The solution obtained by heating the latter with 3 parts of benzoic anhydride at 230—240° for three hours, on cooling to about 120° deposited crystals, which were collected, washed with fused benzoic anhydride, and finally with alcohol.† The hydrolysis of this compound, which required

* This was too trifling for examination. On heating with sulphuric acid it gave a deep olive-green solution.

† This reaction is a general one, acetic anhydride being evolved. Thus acetanilide at 260° gives benzanilide (Found, N=7·1 per cent.). Acetyl-β-naphthol yields the benzoyl derivative at 220° (m. p. 206°), (Found, C=82·14; H=5·03), and is isolated by removing excess of benzoic anhydride with steam distillation, followed by washing with dilute alkali. Dibenzoylalizarin, m. p. 177—178° (Found, C=75·14; H=3·73), and pentabenzoylquercetin, m. p. 187—188° (Found C=72·77; H=3·59), were readily prepared in this manner from the corresponding acetyl compounds.

considerable care, otherwise darkening occurred, was carried out as follows: One gram of the benzoyl derivative was dissolved by gentle warming in 3 c.c. of sulphuric acid, the solution heated at 60° for two hours, and after remaining overnight, diluted with four volumes of acetic acid and briskly boiled. The milky liquid quickly became clear, and crystals of the oxonium sulphate separated. These were collected, hydrolysed by water, and converted into the acetyl derivative, which now melted at 278—280°.

Having now ascertained the characteristics of the pure substance, a more economical method of purification was devised. The purified acetyl derivative was made into a cream with nitrobenzene containing a little acetic anhydride, and the mixture heated until solution was obtained. When cold, the crystals were collected, washed with nitrobenzene followed by acetic anhydride, and hydrolysed by sulphuric acid in the presence of acetic acid. The oxonium sulphate which thus separated was washed with acetic acid, decomposed by water, and the colloidal mass of free colouring matter drained, made into a cream with alcohol, and gently poured into a very large volume of boiling alcohol. A part of the substance without dissolving thus became crystalline, and by evaporating the filtrate to about one-sixth of its bulk, a further quantity separated from the boiling liquid. In the crystalline condition it is almost insoluble in boiling alcohol, and for further purification if necessary the acetyl derivative was employed. For analysis it was dried at 160°.*

Found: C = 55·35; H = 1·98.

$C_{21}H_8O_{12}$ requires C = 55·74; H = 1·77 per cent.

These figures closely approximate with those required by ellagic acid, $C_{14}H_6O_8$ (C = 55·62; H = 1·98), but for reasons given later the higher formula is adopted.

This colouring matter, for which the name *flavogallol* is proposed, forms fine, hair-like, canary-yellow needles, which when heated to a high temperature carbonise without melting, with the production of a trace of a yellow sublimate. It is very sparingly soluble in the usual solvents, and dissolves in 10 per cent. sodium hydroxide solution with an orange-yellow colour, which slowly becomes brown by oxidation. With very dilute alkali a pure yellow coloration is produced. Alcoholic lead acetate gives an orange precipitate, and ferric chloride a dull green liquid, whereas sulphuric and nitric acids respectively give yellow and orange-coloured solutions. By means of the latter it does not give the Griessmayer

* When air dried it contains $4H_2O$. (Found H_2O = 11·3, 11·38. $C_{21}H_8O_{12}$, $4H_2O$ requires H_2O = 11·57 per cent.)

reaction. On mordanted woollen cloth it dyes shades of a purer character than those given by the crude paste:

Chromium.	Aluminium.	Tin.	Iron
Old gold.	Pale brownish-yellow.	Pale greenish-yellow.	Brownish-grey.

When flavogallol, in the form of a paste with alcohol, is boiled with a 25 per cent. solution of potassium acetate in alcohol for three hours an orange-coloured, crystalline powder is obtained, and this is washed with alcohol and dried at 160°.

Found: K = 20·13.

$C_{21}H_5O_{12}K_3$ requires K = 20·67 per cent.

This tripotassium salt dissolves in hot water, giving an orange-yellow solution, which gives with acids a precipitate of flavogallol. Concentrated boiling aqueous potassium acetate behaves similarly, giving at first a curdy, yellow precipitate of fine needles (Found, K = 13·61), which appears to be a mixture of mono- and di-potassium salts, and eventually a tripotassium compound (Found, K = 20·48). The solution of the latter gives respectively with barium chloride and lead acetate yellow and orange precipitates.

Flavogallol anhydrosulphate can be obtained from the acetyl compound, or by adding glacial acetic acid to a solution of flavogallol in sulphuric acid. The product is collected and washed with acetic acid.

Found: C = 46·91; H = 2·42.

$C_{21}H_6O_{11},H_2SO_4$ requires C = 47·36; H = 1·50 per cent.

It crystallises best when obtained from the benzoyl compound by the method above described, and thus forms a glistening mass of orange-yellow prisms. By the action of cold water it is readily transformed into flavogallol and sulphuric acid.

Found, $C_{21}H_8O_{12}$ = 84·26, 84·88; H_2SO_4 = 18·73, 18·70.

$C_{21}H_6O_{11},H_2SO_4$ requires $C_{21}H_8O_{12}$ = 84·96; H_2SO_4 = 18·42 per cent.

Flavogallol does not yield a hydrochloride in the usual manner with 33 per cent. hydrochloric acid, but with hydriodic acid (D 1·7) the formation of a very unstable hydriodide appears to take place.

Acetylflavogallol, $C_{21}H_2O_{12}(C_2H_3O)_6$, consists of small, prismatic needles possessing a faint yellow colour. When slowly heated it melts and decomposes at 278—280°.

Found: C = 56·11, 56·00; H = 3·17, 3·00.

$C_{33}H_{20}O_{18}$ requires C = 56·25; H = 2·84 per cent.

It is sparingly soluble in acetic anhydride, which either alone or in conjunction with nitrobenzene forms the only solvent from which it can be satisfactorily crystallised. Alcohol or acetic acid,

for reasons to be given later, must not be employed in this operation. Its solution in acetic anhydride possesses a pale blue fluorescence.

The acetyl groups in this compound were determined by a modification of the acetic ether method, the indirect process proving to be unsuitable. Being but slowly hydrolysed in the ordinary way, the substance was first dissolved in sulphuric acid, and the solution then rapidly admixed with the alcohol.

Found: $C_2H_4O_2$=51·06, 50·73.

$C_{21}H_2O_{12}(C_2H_3O)_6$ requires $C_2H_4O_2$=51·13 per cent.

Benzoylflavogallol, $C_{21}H_2O_{12}(C_7H_5O)_6$, separates from its solution in benzoic anhydride in small, canary-yellow prisms, which melt at 326—328°, and are sparingly soluble in the usual solvents.

Found: C=70·00, 70·40; H=3·00, 3·25.

$C_{63}H_{32}O_{18}$ requires C=70·26; H=2·97 per cent.

These figures, therefore, correspond with those given by the acetyl determinations, and indicate the presence of six hydroxyl groups. The benzoyl compound was soluble in warm naphthalene, and did not separate, at least to any extent, on cooling, except after a considerable period:

0·5143, in 10·82 naphthalene, gave Δt − 0·300. M.W.=1109.

$C_{63}H_{32}O_{18}$ requires M.W.=1076.

This result is thus in fair agreement with the formula, $C_{21}H_8O_{12}$, assigned to flavogallol.

Flavogallolanilide, $C_{21}H_7O_{11}\cdot NH\cdot C_6H_5$.—When flavogallol is heated with boiling aniline, the gelatinous product at first obtained gradually changes into minute crystals. After digestion for one hour the product was collected and washed with alcohol.

Found: C=61·46; H=2·49; N=3·14.

$C_{27}H_{13}O_{11}N$ requires C=61·48; H=2·46; N=2·65 per cent.

It consisted of yellow needles possessing a slightly more orange tint than flavogallol, which melted at above 345°. It was soluble in dilute alkali hydroxides with an orange-yellow coloration.

Flavogallonic Acid.

When acetylflavogallol is hydrolysed by the acetic ether method, the residual alcoholic liquid on treatment with water deposits after several hours faintly yellow nodules. By recrystallisation from dilute alcohol it was obtained in fine needles.

Found: C=54·79, 55·05; H=3·17, 3·00; Et=5·69.

$C_{23}H_{14}O_{13}$ requires C=55·42; H=2·81; Et=5·82 per cent.

This compound, for which the name *ethyl flavogallonate* is sug-

gested, melts at above 300°, and when dried at 160° is hygroscopic. Dilute alkali hydroxides dissolve it with a pale yellow coloration. Its formation evidently arises from hydrolysis, a lactone group being thus opened, and the carboxyl group subsequently undergoing esterification.

Acetyl Derivative.—The ester was digested with boiling acetic anhydride and a little pyridine, and the crystals which separated overnight were redigested with acetic anhydride. On adding alcohol, prismatic needles were deposited which melted at 214°.

Found: C = 56·22, 56·00; H = 3·99, 3·70.

$C_{37}H_{28}O_{20}$ requires C = 56·06; H = 3·54 per cent.

It is readily soluble in acetic anhydride, and sparingly so in alcohol. When acetylflavogallol is dissolved in acetic anhydride and alcohol is added to the solution, it is reprecipitated at first, but afterwards slowly passes into solution. In order to study this reaction a solution of the acetyl compound in acetic anhydride was boiled for one hour with addition of alcohol, the liquid evaporated, and the viscid residue repeatedly boiled with small quantities of alcohol. The product, which crystallised on keeping, was purified by means of alcohol and acetic anhydride. (Found, C = 56·16; H = 4·02.) It melted at 215—217°, and consisted of the acetylflavogallonic ester described above.

The *acetyl methyl ester* was prepared in the same manner, employing methyl alcohol, and was purified by crystallisation from a mixture of alcohol and benzene.

Found: C = 55·50; H = 3·58.

$C_{36}H_{26}O_{20}$ requires C = 55·52; H = 3·31 per cent.

It formed small, prismatic needles melting at 181—183°.

Flavogallonic Acid.—When flavogallol is added to boiling 30 per cent. potassium hydroxide solution, preferably diluted with a little alcohol to lower the boiling point, the liquid soon loses its colour, a property which is also possessed by the ellagic acid group of colouring matters. By cautious acidification with hydrochloric acid a grey-coloured precipitate is deposited, which is removed, and from the filtrate colourless needles slowly separate. These gradually become greyer in colour, and when dried at 160° are somewhat hygroscopic.

Found: C = 53·35; H = 2·63.

$C_{21}H_{10}O_{13}$ requires C = 53·61; H = 2·13 per cent.

It melts above 300° and dissolves in very dilute alkali hydroxides with a pale yellow colour, becoming browner on keeping in air. Acetic anhydride in the presence of pyridine readily yields an acetyl compound crystallising in prisms which melt at 278—280°,

and have all the properties of acetylflavogallol. (Found, C=56·20; H=3·22.)

The re-formation of the lactone group originally opened by the action of the alkali thus occurs in the presence of boiling acetic anhydride, and a similar result is produced by digesting flavogallonic acid with sulphuric acid in the presence of boiling acetic acid. Anhydroflavogallol sulphate gradually separates, which can be transformed into flavogallol by the action of water.

Interesting is the behaviour of acetylflavogallol with boiling acetic acid, for although at first it remains almost insoluble, a solution is slowly produced, and from this on cooling no separation occurs. The product, which has only been isolated as an amorphous powder, is of a readily soluble nature, and consists probably of acetylflavogallonic acid. With sulphuric and acetic acid anhydroflavogallol sulphate separates. For these reasons alcohol and acetic acid cannot be used in the purification of acetylflavogallol, and the ignorance of these facts caused much inconvenience during the earlier stages of this work.

Flavogallone.

If flavogallonic acid or flavogallol itself (2 grams) is digested with boiling 50 per cent. potassium hydroxide solution for about ten minutes, avoiding air oxidation, cautious acidification causes the deposition of a grey-coloured precipitate, which according to the concentration may be amorphous, or consist of minute needles (1·43 grams). The dried product when acetylated yielded an acetyl derivative in the form of leaflets which were readily soluble in acetic anhydride and melted at 257—259°.

Found: C=56·88; H=3·58.

$C_{34}H_{24}O_{18}$ requires C=56·66; H=3·33 per cent.

A solution of the acetyl compound in boiling acetic acid was hydrolysed by the gradual addition of 33 per cent. hydrochloric acid, causing the separation of a colourless precipitate, which was washed and dried at 160°.

Found: C=56·10; H=2·65.

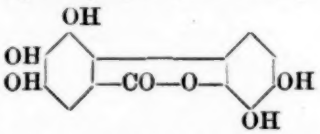
$C_{20}H_{10}O_{11}$ requires C=56·33; H=2·34 per cent.

Flavogallone melts at above 340° and is sparingly soluble in the usual solvents. In absence of air its solution in 10 per cent. sodium hydroxide is almost colourless, but by oxidation passes through yellowish-green to brownish-red. It is insoluble in cold sulphuric acid, but on heating an orange-yellow liquid is produced, which later develops a fine magenta-violet colour; this on dilution with water gives a blue-coloured precipitate. With alcoholic ferric

chloride a pure blue solution is obtained, whereas alcoholic lead acetate yields a pale yellow precipitate.

Whereas flavogallonic acid is produced from flavogallol by the opening of a lactone group, flavogallone is evidently derived from the former by an elimination of its carboxyl group, thus:

This reaction is analogous to that given by ellagic acid, which in these circumstances is transformed into the 2:2′-lactone of 4:5:6:2′:3′:4′-hexahydroxydiphenyl-2-carboxylic acid:



When flavogallone is prepared in the above-described manner, the alkaline liquid before neutralisation, when diluted with water, develops a fine magenta-violet colour, which eventually becomes brown. This is not a property of flavogallone itself, but is proof of the presence of a lactone group in this substance, which is opened by the action of the strong alkali, but closed when the solution is rendered acid. It accordingly appeared probable that flavogallol contains two lactone groups.

Flavogallone is but little attacked by prolonged boiling with potassium hydroxide solution, and suitable conditions for the production of a further degradation product have as yet not been ascertained. Potassium hydroxide at 200—220° yields a brown product very readily soluble in water, and from this no definite compound could be isolated.

Methylation of Flavogallol.

Flavogallol (5 grams) suspended in a mixture of 50 c.c. of methyl alcohol and 10 c.c. of water was treated with equivalent amounts of 40 per cent. methyl-alcoholic potassium hydroxide and methyl sulphate until little or no coloration was produced on addition of the former. The mixture was boiled from time to time, but the process, which occupied about an hour, was tedious, and a very large amount of the reagents was necessary. The product was diluted with water, causing the separation of a viscid mass, and this was removed by shaking with ether. After washing with dilute sodium hydroxide solution, the ethereal liquid was evaporated, and the residue, which slowly crystallised, was digested with boiling 5 per cent. alcoholic potassium hydroxide until a sample of

the liquid no longer became turbid on addition of water. By acidification an oily deposit was obtained, which hardened on keeping, and this was washed, well drained, and dissolved in boiling alcohol. Crystals (2 grams) slowly separated, which were purified by recrystallisation.

Found: C = 57·75; H = 5·16; Me = 23·1, 22·9.

$C_{21}H_4O_5(OMe)_{10}$ requires C = 57·58; H = 5·27; Me = 23·21 per cent.

This compound, which is produced from flavogallol by the addition of three molecular proportions of water and subsequent methylation of ten hydroxyl groups, crystallises in colourless prisms which melt at 206—208°. Sulphuric acid dissolves it to form a colourless liquid which, when heated, develops a fine magenta-red tint, and this by dilution with water gives a deep blue solution (compare flavogallone). A cold alkaline solution does not decolorise permanganate.

The hydriodic acid liquid from the Zeisel determination contained crystals which, when recovered in the usual manner, were found to consist of flavogallol, in that they yielded the acetyl derivative melting at 278—280°.

Employing $N/10$-sodium hydroxide, two samples of the substance required respectively 12·4 and 12·5 per cent. of sodium hydroxide for neutralisation, indicating the presence of two carboxyl groups. [$C_{29}H_{32}O_{11}(CO_2H)_2$ requires NaOH = 12·38 per cent.]

The acid was esterified in the usual manner, and the solution allowed to evaporate in a vacuum. Colourless plates of considerable size gradually separated, which melted at 128—130°.

Found: C = 58·5; H = 5·6; Me = 26·36.

$C_{29}H_{32}O_{11}(CO_2Me)_2$ requires C = 58·75; H = 5·63; Me = 26·7 per cent.

The acid melting at 206—208° (1·2 grams) was unaffected by long digestion with a 7 per cent. potassium hydroxide solution at the boiling point, 1·05 grams being recovered, and the action of concentrated alcoholic potassium hydroxide in sealed tubes at 175° was therefore studied. On cooling, a semi-solid, crystalline product was obtained, and this was dissolved in water, the alcohol evaporated, and when cold the solution was neutralised. No deposition occurred, but on gently boiling crystals gradually separated in considerable amount. These were collected, dissolved in boiling water, and the small quantity of substance which crystallised on cooling and contained some unattacked compound was neglected. The filtrate on evaporation gradually deposited glistening leaflets, which were collected and dried at 160°.

Found: C = 56·96; H = 5·09; Me = 20·90.

$C_{30}H_{32}O_{15}$ requires C = 56·96; H = 5·06; Me = 21·20 per cent.

It melts at 183—184°, and when dried in the air contained one molecule of water of crystallisation.

Found: $H_2O = 2{\cdot}73$.

Theory requires $H_2O = 2{\cdot}77$ per cent.

The hydriodic acid liquid from the Zeisel determination contained flavogallol, which was identified by the acetyl derivative melting at 278—280°.

Titration indicated the presence of two carboxyl groups.

Found: NaOH = 12·92.

$C_{28}H_{30}O_{11}(CO_2H)_2$ requires NaOH = 12·34 per cent.

By the action of alcoholic potassium hydroxide on the acid $C_{21}H_4O_5(OMe)_{10}$ (m. p. 206—208°), one methoxy-group is therefore hydrolysed, with the formation of the acid $C_{21}H_5O_6(OMe)_9$. With hot sulphuric acid the latter acid gives, like the former, a magenta-red solution passing to blue on dilution with water.

The alcoholic mother liquors from the crude methylation product, which had deposited the acid melting at 206—208°, when gradually evaporated, gave crystals which, after purification with the same solvent or from acetic acid, heated at 238—240°.

Found: C = 57·26; H = 5·29; Me = 22·73.

$C_{21}H_4O_5(OMe)_{10}$ requires C = 57·58; H = 5·27; Me = 23·21 per cent.

From alcohol when slowly crystallised it forms large prisms, which contain alcohol of crystallisation. This is slowly evolved on keeping, the crystals becoming opaque.

Found at 160°: $C_2H_6O = 6{\cdot}49$.

$C_{31}H_{34}O_{15},C_2H_6O$ requires $C_2H_6O = 6{\cdot}64$ per cent.

When heated with sulphuric acid it behaves similarly to the acid melting at 206—208°, a magenta-red solution being obtained which passes to blue when diluted with water. Its cold alkaline solution does not reduce permanganate.

Titration indicated the presence of two carboxyl groups.

Found: NaOH = 12·62.

Theory requires NaOH = 12·38 per cent.

The hydriodic acid liquid from the Ziesel determination appeared to contain crystals of flavogallol, in that these yielded an acetyl derivative melting at 278—280°.

The *methyl* ester, prepared in the usual manner, was precipitated by water as an oil, the solution of which in dilute alcohol slowly deposited large, prismatic needles. These melted at 86—87°, and were very soluble in alcohol.

Found: C = 58·60; H = 5·64; Me = 26·04.

$C_{29}H_{32}O_{11}(CO_2Me)_2$ requires C = 58·75; H = 5·63; Me = 26·7 per cent.

The acid melting at 238—240° is thus isomeric with that melting at 206—208°, which is simultaneously produced with it by the methylation of flavogallol.

By digestion with boiling 10 per cent. alcoholic potassium hydroxide for six hours, little or no hydrolysis occurred. The main bulk of the recovered substance after crystallisation from dilute alcohol melted at 236—237°, and that isolated from the mother liquors at 233—234°. The action of alcoholic potassium hydroxide at higher temperatures has not yet been studied.

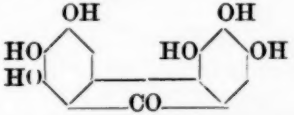
When distilled with zinc dust flavogallol yielded a small amount of an oily hydrocarbon, which did not crystallise on long keeping.

Preliminary experiments on the methylation of flavogallol with diazomethane have yielded a methyl ether crystallising in yellow needles melting at above 305°, and this is reserved for investigation.

The employment of ferric sulphate and manganese dioxide in the presence of sulphuric acid as oxidising agents, to replace arsenic acid, for the production of flavogallol from gallic acid has been studied, but the results have hitherto been unsatisfactory. In the former case ellagic acid in considerable amount is produced, and it seems possible that this may prove to be the most economical method hitherto devised for the preparation of this dyestuff.* The crude substance, however, contains traces of iron, but this can be readily removed by the preparation of the acetyl derivative.

Note on Hexahydroxybenzophenone.

In the earlier stages of this work it was considered possible that a compound having the formula:



might be formed. Biginelli (*Gazzetta*, 1909, **39**, ii, 68) states that among other products dihexahydroxybenzophenonearsinic acid is formed by the interaction of arsenic and gallic acids. Such a compound might presumably be formed by the oxidation of hexahydroxybenzophenone, although, as experiment indicated that flavogallol does not result from such a process, the product of the reaction was not carefully examined. The details for the preparation of hexahydroxybenzophenone are (D.R.-P. 49149) not to be found in the literature, but it was ascertained that the following process gives good results: One part of gallic acid, 1 part of pyro-

* A provisional patent for this process has been secured.

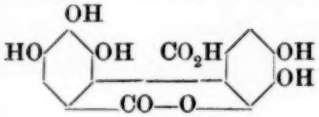
gallol, and 3 parts of zinc chloride are heated at 120°. From the product the ketone is precipitated by means of water, and is recrystallised from water with the employment of animal charcoal. It consists of faintly yellow needles melting at 272—273°. (The above patent gives "above 270°.") (Found, C=56·15; H=3·65 per cent.) The *acetyl* derivative not previously described crystallises in needles melting at 132°.

Found: C=56·66; H=4·25.

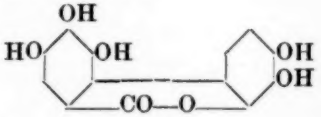
$C_{25}H_{22}O_{13}$ requires C=56·60; H=4·15 per cent.

Summary.

It seems clearly established from the composition of the potassium salt, $C_{21}H_5O_{12}K_3$, and of the anhydrosulphate, $C_{21}H_6O_{11},H_2SO_4$, and also from the molecular weight determination of the benzoyl derivative, that flavogallol possesses the formula $C_{21}H_8O_{12}$. It contains apparently also six hydroxyl groups, and the percentage of these, as indeed the percentage composition of flavogallol itself, it is interesting to note, are almost the same as those of ellagic acid itself. A further resemblance between flavogallol and ellagic acid is shown by their behaviour with boiling concentrated alkali hydroxide solutions, for whereas flavogallonic acid, $C_{21}H_{10}O_{13}$, and flavogallone, $C_{20}H_{10}O_{11}$, are produced from the former, luteoic acid (I) and the 2:2′-lactone of 4:5:6:2′:3′:4′-hexahydroxydiphenyl-2-carboxylic acid (II) are yielded by the latter:

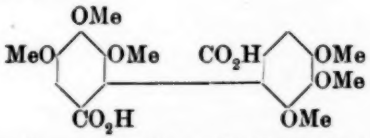


(I.)



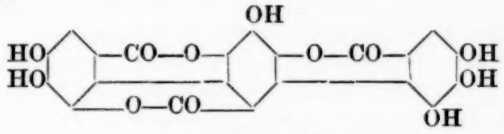
(II.)

With methyl sulphate and alkali and hydrolysis of the ester, ellagic acid gives the acid:



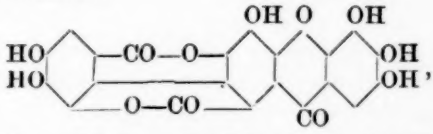
which is closely analogous to the acid $C_{29}H_{32}O_{11}(CO_2H)_2$ produced in the same way from flavogallol. On the other hand, flavogallol gives the sulphate referred to above, whereas oxonium sulphates of the ellagic acid group cannot be prepared, at least in the usual manner. Again, flavogallol differs from ellagic acid in being yellow and in possessing strong dyeing properties towards mordants. That flavogallol may possibly be produced from ellagic acid by condensation with a molecule of gallic acid seems feasible, not only on

account of its formula, but from the fact that during its preparation some ellagic acid is always produced. Important is the fact that whereas during methylation galloflavol takes up three molecules of water, a dicarboxylic acid only is formed, for this not only precludes the presence of a free carboxyl group in the colouring matter itself, but its possession of the following semi-symmetrical constitution:



which at one time was apparently feasible. On the other hand, it seems probable that a pyrone group is present in flavogallol, and that this during the somewhat drastic methylation process is opened, and thereby takes up the third molecule of water under discussion,

with subsequent methylation. If such is the case the following formula can be devised:



which assumes the oxidation of gallic acid to tetrahydroxybenzoic acid and its subsequent condensation with ellagic acid. This constitution explains the main properties of flavogallol, but cannot be considered completely satisfactory until the relationship of the isomeric acids simultaneously produced during the methylation process has been elucidated. Should this prove to be a case of geometrical isomerism, the formation of flavogallol from gallic acid will be of a more complex nature than is above conjectured, and its true nature will still involve investigation of a prolonged character.

Unfortunately, owing to other duties, further work on the subject may be delayed for some time, but it is desired to reserve the study of this substance, which will be again undertaken when opportunity occurs.

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[*Received, March* 31*st*, 1916.]

XLII.—*The Colour of Polyhydroxyanthraquinone Dyes.*

By David B. Meek and Edwin Roy Watson.

It has been suggested by us (T., 1915, **107**, 1567 *et seq.*) that the vibration causing the colour of dyes is a change, or tendency to change, from one quinonoid form to another, involving alternation of double and single bonds along a conjugate chain. It was shown that where such dyes were chosen with similar structure but with conjugate chains of different lengths the wave-lengths of the maxima of absorption were in the ratio of the lengths of the chains of double and single bonds. In that investigation the chains of double and single bonds differed only in length. The present work was undertaken with the object of ascertaining why the multiplication of auxochromes in a dye molecule deepens the colour. This is an empirical rule which is true for many groups of dyes, and in the anthraquinone group in particular the multiplication of auxochromes has led to the production of some very valuable dyes.

From the point of view of the theory already mentioned, the results now obtained may be considered as throwing light on the effect of varying the nature of the conjugate chains whilst keeping their lengths unaltered. We may consider that the chains have been varied in two ways, namely, (1) by changing the end-groups, for example, by observing the behaviour of alizarin, etc., in alcohol, in potassium hydroxide, and on different mordants; (2) by varying the number and positions of the attached auxochromes throughout the chains, for example, by considering the absorption of alizarin, quinizarin, etc., under the same conditions, say, all in alcohol or all in potassium hydroxide solution, etc.

No. (1) has led to the discovery of a very definite relationship between the absorption spectra of the dyes themselves in neutral solvents and the absorption spectra of their salts, and a hypothesis has been suggested to explain this relationship. No. (2) has not led as yet to any simple relationship between the absorption spectra of the dyes and the number and positions of the contained auxochromes, but it has yielded experimental evidence which is not in complete concordance with various hypotheses suggested by other investigators.

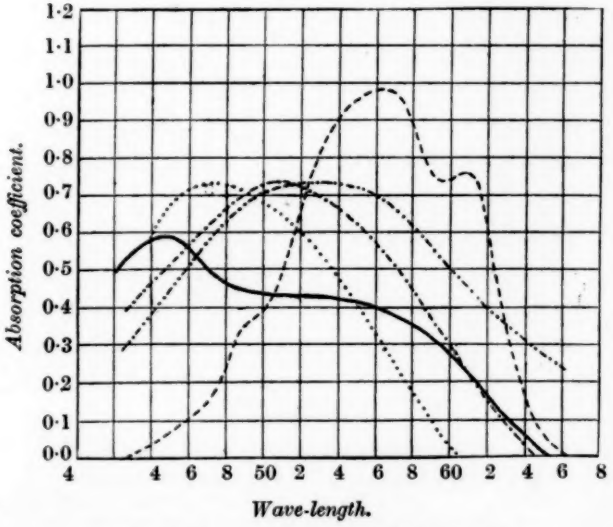
Experimental.

In this investigation the absorption spectra were observed for the visible spectrum only, and the instrument used was a Nutting

spectrophotometer in conjunction with a large model wave-length spectrometer both by Adam Hilger, London. The substances chosen for examination were:

(1) Alizarin, 1:2-dihydroxyanthraquinone.
(2) Quinizarin, 1:4-dihydroxyanthraquinone.
(3) Purpurin, 1:2:4-trihydroxyanthraquinone.
(4) Anthragallol, 1:2:3-trihydroxyanthraquinone.
(5) Alizarin-Bordeaux, 1:2:5:8-tetrahydroxyanthraquinone.
(6) Alizarin-cyanine, 1:2:4:5:8-pentahydroxyanthraquinone.
(7) Anthracene-blue, W.R., 1:2:4:5:6:8-hexahydroxyanthraquinone.
(8) Rufigallol, 1:2:3:5:6:7-hexahydroxyanthraquinone.

FIG. 1.



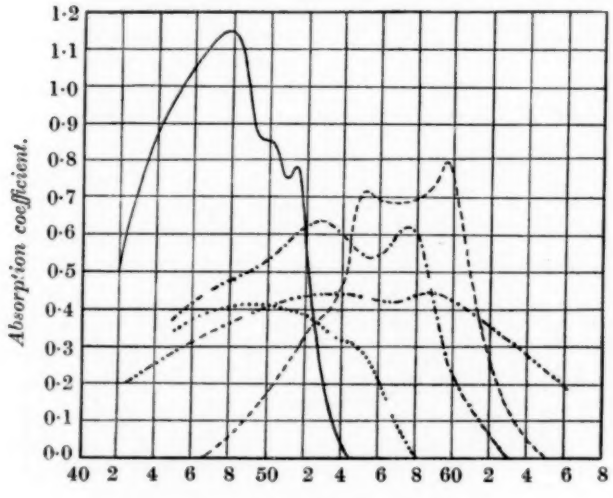
Alizarin or 1:2-*dihydroxyanthraquinone.*

———— *Alizarin in alcohol, N/10⁴, 10 mm. thickness.*
— — — — „ „ KOH, *N*/10⁴, 10 *mm. thickness*, 400 *mols.* KOH.
. . . . . „ *on tin mordanted wool, ¼ per cent. dyeing.*
— · — · — „ „ *alum* „ „ „ „ „
— · · — · · „ „ *chrome* „ „ „ „ „

The absorption spectrum of each of these dyes was examined (1) in alcoholic solution, (2) in aqueous potassium hydroxide solution, and on wool mordanted with (3) tin, (4) alum, and (5) chrome respectively. In the Nutting spectrophotometer there are two apertures, one to receive the light the spectrum of which has to be examined, and the other to receive the comparison light from the same source. By placing two fabrics at 45° to the axis of the

instrument and allowing the light from the dyed fabric to enter one aperture and the light from the undyed mordanted fabric to enter the other aperture, the absorption spectrum of the dyed fabric was obtained. For fabrics, a carbon arc lamp was required as source in order to raise the intensity of light to such a degree that measurements could be made easily. The mordant of the undyed comparison fabric used was always the same as the mordant of the dyed fabric being examined. In all cases where the colour

FIG. 2.



Quinizarin or 1 : 4-*dihydroxyanthraquinone.*

———— *Quinizarin in alcohol, N/10⁴, 10 mm. thickness.*
— — — — „ „ KOH, N/10⁴, 10 *mm. thickness,* 400 *mols.* KOH.
. . . . . „ *on tin mordanted wool* 1 *per cent. dyeing.*
— · — · — „ „ *alum* „ „ „ „
— · · — · · „ „ *chrome* „ „ „ „

of a solution was fugitive, sets of time readings were taken, and the observed absorption curves were corrected for fading. To the best of our knowledge, this is the first recorded investigation of the absorption spectra of dyes on the fabric. It is the colour of the dye on the fabric which is of technical value, and, as is well known, many dyes give quite different colours on the fabric from what they exhibit in alcoholic, alkaline, or acid solution, and frequently the same dye gives very different colours on different mordants.

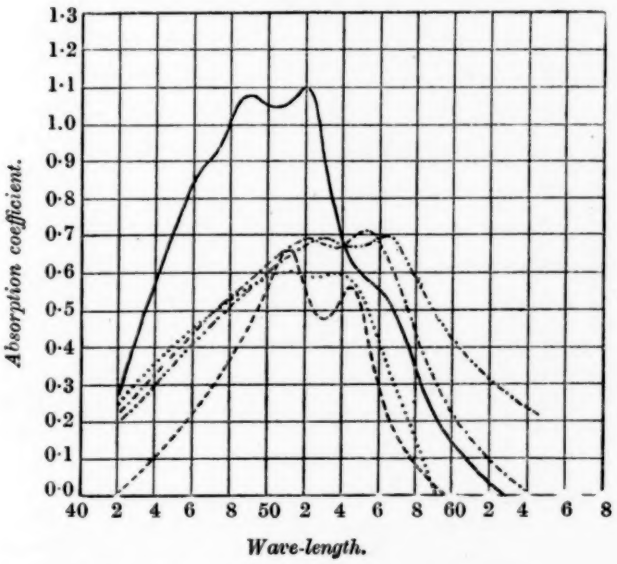
Figs. 1 to 8 give the observed curves. The two points which will be discussed in relation to these curves are:

(1) The change of the absorption spectrum of each dye as the conditions are varied.

(2) The change of the absorption spectra of the group of dyes in relation to the number and position of auxochromes.

The absorption spectra were first examined (E. R. W.) with a Brace spectrophotometer modified by one of us (D. B. M.), and the results obtained seemed to indicate a simple relation between the spectra examined, which also offered a mechanical explanation of the regularities already noticed in ocular observations. Accord-

FIG. 3.



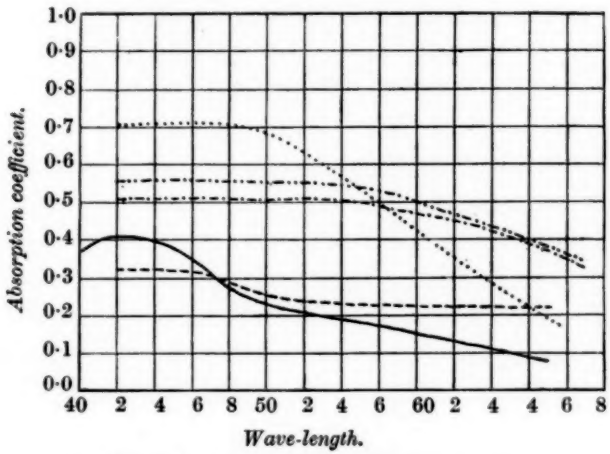
Purpurin or 1 : 2 : 4-*trihydroxyanthraquinone.*

——— ——— *Purpurin in alcohol, N/10⁴, 10 mm. thickness.*
— — — — „ „ KOH *N*/10⁴, 10 *mm. thickness*, 400 *mols.* KOH.
. . . . . „ *on tin mordanted wool ¼ per cent. dyeing.*
— · — · — „ „ *alum* „ „ „ „
— · · — · · „ „ *chrome* „ „ „ „

ing to this interpretation, the absorption spectra of all the dyes of this group consist of two bands, one at about $\lambda = 5000$ and the other at about $\lambda = 7000$; the wave-length of these bands is somewhat increased by the multiplication of auxochromes; the relative intensity of the band of longer wave-length is increased when there are two hydroxyl groups in the *o*- or *p*-positions with respect to one another in the nucleus; the relative intensity is still more increased when the *o*- or *p*-grouping occurs in both nuclei, or when

three hydroxyl groups occur in the 1:2:4-position in one nucleus. The 1:2:3-grouping of the three hydroxyl groups in one nucleus causes an almost equal development of the two bands, the result being a brown colour. Further, the relative development of the two bands depends on the condition under which the dye is examined, the band of shorter wave-length being prominent in alcoholic solution, and that of longer wave-length being developed more and more in the salts according to the basicity of the metal with which the dye is combined. This seemed to indicate two different tautomeric forms or modes of vibration, that producing

FIG. 4.



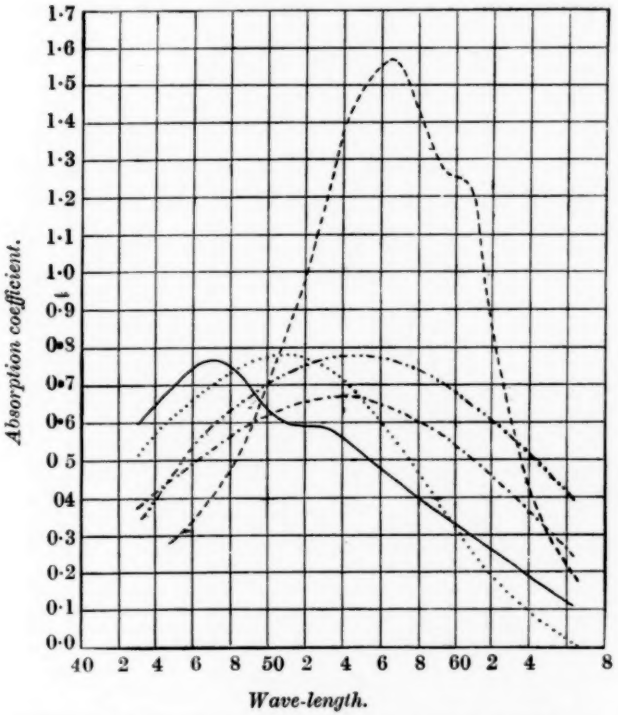
Anthragallol or 1:2:3-*trihydroxyanthraquinone.*

———— *Anthragallol in alcohol, N/10⁴, 10 mm. thickness.*
— — — — „ „ KOH, *N*/10⁴, 10 *mm. thickness,* 400 *mols.* KOH.
. . . . . „ *on tin mordanted wool ¼ per cent. dyeing.*
— · — · — „ „ *alum* „ „ „ „
— · · — · · „ „ *chrome* „ „ „ „

the band of longer wave-length being in greater proportion when the *o*- or *p*-grouping of the hydroxyl groups occurred and when the dye was in combination with a basic oxide. This interpretation is similar to that already advanced for the phthalein and benzein dyes (Medhi and Watson, T., 1915, **107**, 1581). The present work shows, however, that these observations made the bands very much too broad and also removed all the detail from them. Theoretical curves formed in the manner suggested by compounding two bands of different relative intensities differ from the experimental curves here recorded to a much greater extent than can be explained by any possible experimental error.

In this connexion it may be remarked that the same considerations seem to us sufficient to render untenable the similar hypothesis which Hantzsch (*Ber.*, 1910, **43**, 82) has put forward to explain the various colours which violuric acid and its derivatives and *iso*oxazolone exhibit when in combination with different metals

FIG. 5.



Alizarin-Bordeaux or 1 : 2 : 5 : 8-*tetrahydroxyanthraquinone.*

———— *Alizarin-Bordeaux in alcohol, N*/10⁴, 10 *mm. thickness.*
— — — — " " " KOH, *N*/10⁴, 10 *mm thickness,* 400 *mols.* KOH.
. . . . . *Alizarin-Bordeaux on tin mordanted wool,* ¼ *per cent. dyeing.*
—·—·— " " " *alum* " " " "
—··—·· " " " *chrome* " " " "

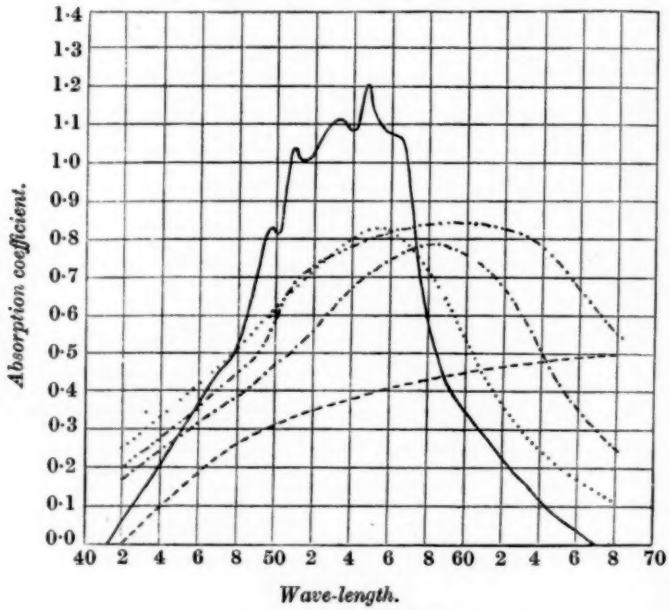
and in different solvents. Its position has been summarised as follows: "The change in colour [as the positive nature of the metallic radicle increases] is attributed to a chemical change, namely, to the passage from the oximino-ketone form to the nitroso-enolic form:

$$\begin{matrix} O{:}C{\cdot}C{:}N{\cdot}OH \\ | \quad | \end{matrix} \longrightarrow \begin{matrix} OH{\cdot}C{:}C{\cdot}NO. \\ | \quad | \end{matrix}$$

All solutions of the salts consist of a mixture of the two forms in dynamic equilibrium, the proportion of each depending on the positive character of the metallic or substituted ammonium radicle present and also on the nature of the solvent."

Take as an example the absorption curves of diphenylvioluric acid and its salts (*Ber.*, 1910, **43**, 666). According to the hypothesis, the curves for the salts should be obtained by compounding the following two absorption curves in different proportions,

FIG. 6.



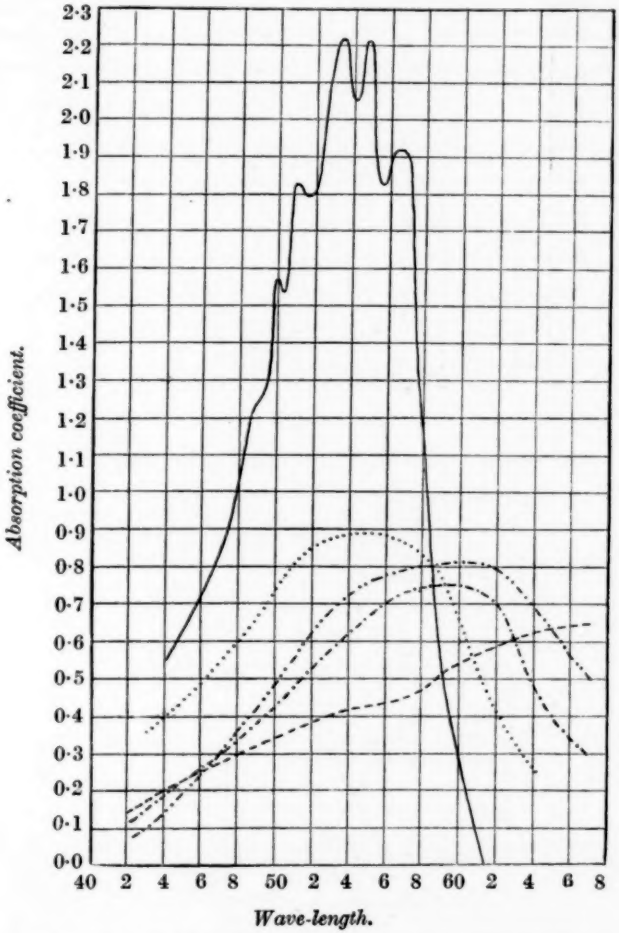
Alizarin-cyanine or 1 : 2 : 4 : 5 : 8-*pentahydroxyanthraquinone.*

———— *Alizarin-cyanine in alcohol, N*/10⁴, 10 *mm. thickness.*
— — — — „ „ „ KOH, *N*/10⁴, 10 *mm. thickness,* 400 *mols.* KOH.
. . . . . *Alizarin-cyanine on tin mordanted wool,* ¼ *per cent. dyeing.*
—·—·— „ „ „ *alum* „ „ „ „
—··—·· „ „ „ *chrome* „ „ „ „

namely, the absorption curve for the pure oximino-ketonic form which may be taken to have its maximum at frequency 1500, and the curve for the pure nitroso-enolic form which has its maximum at 3800. The curve for the cæsium salt in acetone solution has its maximum at 1700, that for the lithium salt in acetone has its maximum at 1950, and that for the lithium salt in ethyl acetate has its maximum at 3250. It is possible to compound bands at

frequencies 1500 and 3800 in such different proportions as to give resultant bands with maxima at the required frequencies, 1700.

FIG. 7.



Anthracene-blue or 1 : 2 : 4 : 5 : 6 : 8-*hexahydroxyanthraquinone.*

———— *Anthracene-blue in alcohol, N/10⁴, 10 mm. thickness.*

— — — — „ „ „ KOH, *N*/10⁴, 10 *mm. thickness,* 400 *mols.* KOH.

. . . . . *Anthracene-blue on tin mordanted wool ¼ per cent. dyeing.*

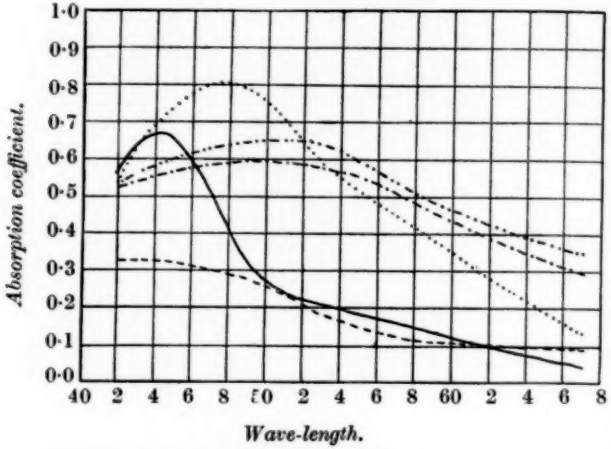
— · — · — „ „ „ *alum* „ „ „ „

— · · — · · „ „ „ *chrome* „ „ „ „

1950, and 3250, but the fundamental bands at 1500 and 3800 must be at least more than 2(3800 – 1500) in breadth, and if such broad

fundamental bands are taken the resultant bands are much broader than those given by direct observation.

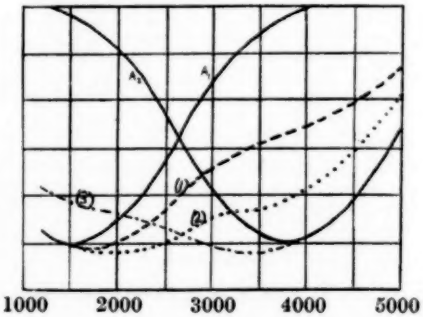
FIG. 8.



Rufigallol or 1 : 2 : 3 : 5 : 6 : 7-*hexahydroxyanthraquinone.*

———— *Rufigallol in alcohol, N/10⁴, 10 mm. thickness.*
— — — — „ „ KOH, *N*/10⁴, 10 *mm. thickness,* 400 *mols.* KOH
. . . . . „ *on tin mordanted wool,* ¼ *per cent. dyeing.*
— · — · — „ „ *alum* „ „ „ „
— · · — · · „ „ *chrome* „ „ „ „

FIG. 9.

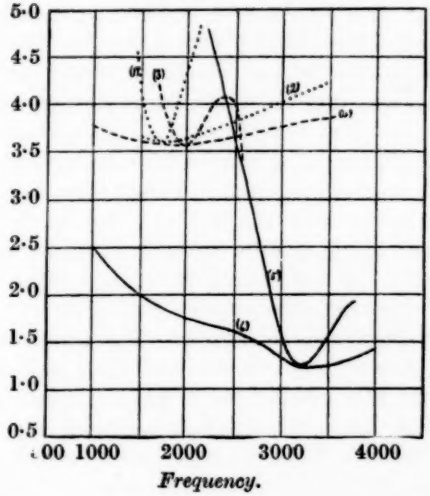


———— A_1 *and* A_2 *are two fundamental bands at frequencies* 1500 *and* 3800.
(1) — — — — *Resultant of* A_1 *and* A_2 *in the ratio of* 10 : 5.
(2) . . . . . „ „ „ „ „ 10 : 8.
(3) — · — · — „ „ „ „ „ 8 : 10.

Fig. 9 shows two fundamental bands, A_1 and A_2, with frequencies at 1500 and 3800 which, taken in the proportions of 10 : 5, 10 : 8,

and 8:10 respectively for intensities, yield the curves (1), (2), and (3) with maxima at frequencies 1700, 1950, and 3250 approximately. These curves, (1), (2), and (3), have been proportionately reduced, so that their maxima coincide with those of Hantzsch's experimental curves, and Fig. 10 shows these reduced curves and the experimental curves together. It will be seen that there is not the slightest coincidence between the theoretical curves and the experimental ones. The theoretical curves are much too broad, and yet if the fundamental curves are taken narrower than those given, the compounding of them in any proportion will not shift the maxima

FIG. 10.



(1), (3) (5) *are Hantzsch's curves for diphenylvioluric acid* (*Ber.*, 1910, **43**, 666).
(1) *Cs salt in acetone solution.*
(3) *Li* „ „ „ „
(5) *Li* „ „ *ethyl acetate solution.*
(2), (4) *and* (6) *are curves compounded from the fundamental bands at* 1500 *and* 3800, *so that the maxima of the resultant curves correspond with those of Hantzsch's three curves.*

from frequencies 1500 and 3800. The well-marked minima at 2150 and 2400 in Hantzsch's curves (1) and (3) are absent from the theoretical curves. The conclusion is that Hantzsch's hypothesis is not in accordance with his own experimental data.

In the case of the anthraquinone dyes, there is much better agreement than this between the experimental curves and the theoretical curves drawn according to this hypothesis, but yet there is a much greater difference than can be explained by experimental error.

Change of the Absorption Spectra when the Conditions are Varied.

On examination of Figs. 1 to 8 it will be observed that a regular change is produced in the absorption spectrum of a dye in passing from alcoholic solution to the various dyeings on tin, alum, and chrome, and finally to the solution in aqueous potassium hydroxide. In all cases, with the exception of purpurin and perhaps also rufigallol, the maxima of the absorption bands or groups of bands are steadily shifted towards the red end of the spectrum on passing from the free dyestuff to its various salts, and the order of the shift agrees with the order of increase of the positive character of the metallic radicle in combination. The variation of the metallic radicle does not alter the length of the conjugate chain of double and single bonds which may be considered as alternating during tautomeric change, and so we are led to consider the character of the metallic radicle as modifying the period of oscillation of a tautomeric change involving a fixed number of double and single bonds. In alizarin the only conjugate chains of double and single bonds which we can imagine as oscillating during tautomeric change have four, three, and two double bonds respectively. If we regard the long chain as responsible for the band at $\lambda=5690$, the shorter chains should give bands at $\lambda=4270$ and $\lambda=2845$ approximately. The solution in potassium hydroxide does show a band at $\lambda=2700$, and the band exhibited in alcoholic solution perhaps might be identified with that predicted at $\lambda=4270$, but without some addition the theory cannot explain the bands observed in the absorption spectra of the dyeings on tin, alum, and chrome which lie between $\lambda=4270$ and $\lambda=5690$. These bands are too close together to be explained as due to conjugate chains of different lengths, as the ratios of their frequencies can only be expressed by whole numbers much larger than the constitutional formula will allow for the number of alternate double and single bonds in the molecule. In short, the closeness of the bands for any one dye under different conditions leads us to the conclusion that these various bands must be due to oscillating conjugate chains of fixed lengths modified by the metallic radicles with which the dye is combined.

If we consider these conjugate chains as in a state of tension, the period of oscillation will be shorter the greater the tension, and the tension will be the greater the more firmly the metallic radicle is combined with the dye. When the dye is combined with a strong positive radicle, the degree of dissociation in solution will be greater than when it is combined with a weak positive radicle. In a partly dissociated compound some molecules have still the

metallic radicle attached to the dye molecule. The greater the dissociation the smaller is the number of molecules which have still the attached metallic radicle. We may regard the electric tubes of force from the metallic atom as partly connecting with the dye molecule and partly radiating around. The larger the dissociation, the smaller will be the number of tubes of force joining the metallic radicle to the dye molecule in those molecules which are undissociated, and the smaller will be the tension in the chain, and therefore the longer will be the wave-length of the maximum of the absorption band. Hence by increasing the positive nature of the radicle, the absorption band should be moved towards the red end of the spectrum. This will be found to be the case with all the dyes examined in this paper, the order being (1) alcoholic solution, dyed fabric (2) tin-, (3) alum-, or (4) chrome-mordanted, and (5) solution in aqueous potassium hydroxide. Purpurin is an exception. The conclusion from this portion is that the more electropositive the nature of the radicle attached to the conjugate chain is the longer will be the wave-length of the maximum of the absorption band.

From examination of the curves in Figs. 1 to 8 some other points may be noted. In several cases, as the radicle is changed the character of the curve remains the same, whilst the band or group of bands moves towards the red end of the spectrum, for example, the pair of bands in quinizarin are retained throughout the varied conditions, and the same also is true with regard to purpurin. In other cases the detail exhibited in the alcoholic solution bands disappears, or tends to disappear, from the absorption spectra on tin, alum, chrome, or potassium hydroxide. The sharp character of the bands also disappears in some cases, the bands becoming shallower and broader as the positive character of the metallic radicle increases, for example, the group of six bands exhibited by alizarin-cyanine in alcohol is changed into one band, which becomes shallower and broader as the positive character of the metallic radicle increases. This is also the case with anthracene-blue W.R. On the other hand, the broad, featureless band of alizarin in alcohol is replaced by two, or even three, bands in potassium hydroxide. There is one point, further, worthy of notice, namely, the intensity of the absorption is of the same order for all the dyes in solution. The same is true for all the dyeings on the fabrics. Owing to the different circumstances, the solutions and the dyeings cannot be compared with each other in this respect.

We may now see how the results obtained agree with Baly's theory (*Phil. Mag.*, 1914, **27**, 632 *et seq.*). According to this theory, each of the maxima observed under these varied conditions

is a definite integral multiple of a fundamental frequency in the infra-red. Take alizarin as an example. The new bands recorded in this paper, considered in addition to those already described by Meyer and Fischer (*Ber.*, 1913, **46**, 74 *et seq.*), would necessitate a reduction of the fundamental frequency and a corresponding increase of the integral multiples, the latter reaching the high figure of at least 57 for the band of highest frequency, thus:

	Cr.	Al.	Sn.	Alcohol.
New bands λ.....	5275	5070	4730	4470
1/λ.....	1920	1980	2130	2230

Introducing these into the series already given (Watson and Meek, T., 1915, **107**, 1575) we get:

Expt.	160—162	180	192—193	198—200
(Calc.)	162	175·5	189	195·75
(Calc.)	6·75×24	6·75×26	6·75×28	6·75×29

Expt.	213	223	303	312	372
(Calc.)	209·25	222·75	303·75	310·5	371·25
(Calc.)	6·75×31	6·75×33	6·75×45	6·75×46	6·75×55

Expt.	376	385
(Calc.)	378	384·75
(Calc.)	6·75×56	6·75×57

The theory is evidently strained to its utmost, and there is little doubt that the study of other salts, for example, those of calcium, strontium, and barium, would give additional maxima and involve further reduction of the fundamental frequency with corresponding increase of the integral multiples.

The Change in the Absorption Spectra produced by Variation of the Number and Position of the Auxochromes.

At the present stage we cannot offer any explanation which will account completely for the way in which the multiplication of auxochromes alters the absorption spectra under similar conditions. The addition of auxochromes does not give any opportunity for changing the length of the conjugate chains of double and single bonds; nor can the addition of auxochromes be considered as merely "weighting" the chain and causing slower vibrations, for, from this point of view, bromine and ethoxy-derivatives of alizarin might be expected to have absorption bands as far into the red as those of the polyhydroxyanthraquinones. This is not the case.

The best that we can do at this stage is to formulate certain general rules which are the result of experiment and observation, without being able to give any explanation of these rules.

Georgievics (*Monatsh.*, 1911, **32**, 329 *et seq.*) has formulated certain generalisations on the influence of hydroxyl groups on the

colour of the "lakes" of these dyes. The results have been summarised as follows: "Hydroxyl groups in the α-positions produce red and blue dyes, in the β-positions yellow and brown dyes; however, an α-hydroxyl group may mask the effect of a β-hydroxyl group, and vice versa. . . . The hydroxyanthraquinones, therefore, are divisible into two groups. One group . . . forming yellow and brown lakes has a para-quinonoid structure, for example, anthragallol . . . whilst the other group, which includes alizarin and its derivatives, forming red or blue lakes (except hystazarin, which occupies an intermediate position), has an ortho-quinonoid structure. . . . In individual hydroxyanthraquinones the tendency to the production of one or other of the quinonoid forms may be such that one and the same dye may be ortho-quinonoid in some lakes and para-quinonoid in others."

These generalisations seem open to criticism on the following grounds:

(1) They do not explain why two hydroxyl groups at least are necessary to produce a red or a blue colour. It may be said that the monohydroxy-derivatives are not mordant dyes, and are therefore not included in the generalisations about lakes. We have shown above, however, that there is a simple relationship between the colour of a dye in alkaline solution and on the various mordants, and consequently Georgievics's generalisations should hold also for the colour of the alkaline solutions of the dyes. From his rules we might expect that 1-hydroxyanthraquinone would be a red or a blue colour, but, as a matter of fact, in alkaline solution it has an absorption band at $\lambda = 4960$ and the colour of the solution is yellow. Alizarin (1:2-dihydroxyanthraquinone), according to his rules, should have the blue colour due to the hydroxyl in the α-position partly masked by the yellow of the hydroxyl in the β-position, but, as is well known, alizarin dissolves in potassium hydroxide with a bluish-violet colour.

(2) They do not explain why 1:4-dihydroxyanthraquinone should have a deeper* colour than 1:5- or 1:8-dihydroxyanthraquinone. Quinizarin (1:4-dihydroxyanthraquinone) is blue in

* In this paper, where the term "deeper" is used in connexion with colour the meaning that has to be attached to it is as follows. One colour will be considered deeper than another if its absorption band is nearer the red end of the spectrum than the absorption band of the other. This may seem a little arbitrary at first sight; but when it is remembered that light reflected from dyed fabrics generally gives an absorption band the breadth of which at half its height is about half the length of the visible spectrum, it will be found that displacement of a band of such a breadth from the blue end of the spectrum to the red end will give a series of colours similar to that generally recognised as increasing in "depth" of colour, namely, yellow, orange, red, violet, blue, and green.

potassium hydroxide solution and has a blue-violet barium salt; anthrarufin (1:5-dihydroxyanthraquinone) is reddish-violet in potassium hydroxide and has a carmine-red barium salt; chrysazin (1:8-dihydroxyanthraquinone) is yellow-red in potassium hydroxide and has a red barium salt.

(3) They do not explain why alizarin should have as deep a colour as quinizarin. According to these rules, the β-hydroxyl should have a prejudicial effect.

(4) They do not explain why alizarin should have a much deeper colour than 1:3-dihydroxyanthraquinone.

(5) They do not explain the deep colour of 2:3-dihydroxyanthraquinone, namely, cornflower-blue in potassium hydroxide, red on alum mordant; the calcium salt is violet, and the barium salt blue.

These criticisms suggest a generalisation which seems much more in harmony with the facts than those of Georgievics, namely:

(*a*) Two hydroxyl groups in one benzene nucleus in the ortho- or para-position with respect to one another are necessary to produce a deep (red, violet, or blue) colour.

(*b*) The colour is still further deepened if both benzene nuclei contain pairs of hydroxyl groups in the *o*- or *p*-position to one another.

(*c*) Three hydroxyl groups in the 1:2:4-positions in one benzene nucleus produce a deeper colour than a pair of hydroxyl groups in the *o*- or *p*-position.

(*d*) Three hydroxyl groups in the 1:2:3-positions in one benzene nucleus produce a brown colour.

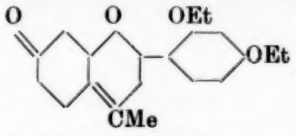
The generalisations bear a marked resemblance to the rules put forward by Kauffmann (Kauffmann and Franck, *Ber.*, 1906, **39**, 2722), and are probably applicable to all groups of dyes, for example, (*a*) the hydroxy-derivatives of azobenzene dissolve in potassium hydroxide with the following colours:

p-Hydroxyazobenzene	Yellow.
o-Hydroxyazobenzene	Yellow.
Benzeneazoresorcinol	Orange.
Benzeneazocatechol	Carmine.
Benzeneazoquinol	Blue.
Benzeneazopyrogallol	Brick-red.

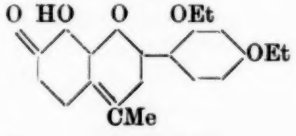
(*b*) Fluorescein, quinolphthalein, and catecholphthalein dissolve in potassium hydroxide with a yellow colour, hydroxyquinolphthalein gives a cherry-red, gallein a blue, and phloroglucinolphthalein an orange under the same conditions.

(*c*) In the pyranol series of dyes (prepared partly by Bülow and partly by Watson and Sen) the effect of two hydroxyl groups in

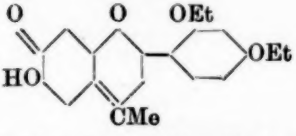
the ortho-position with respect to one another in the benzo-group can be seen from the following comparison:

(1) 

Gives redder and yellower dyeings than alizarin brown.

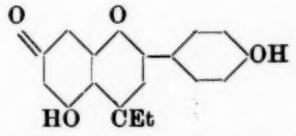
(2) 

Green with sodium alkyloxide, blue in pyridine. Olive green dyeings on chrome.

(3) 

Dark red with alcoholic potassium hydroxide,

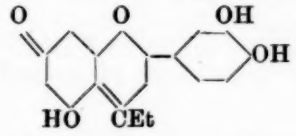
The less favourable effect, so far as depth of colour is concerned, of two hydroxyl groups in the *m*-position with respect to one another in the benzo-group can be seen by comparing the preceding with:

(4) 

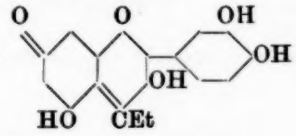
Crimson with potassium hydroxide, gives brownish-orange dyeings.

The extra hydroxyl group in the phenyl group cannot counterbalance the unfavourable effect of the meta-grouping in the benzo-nucleus.

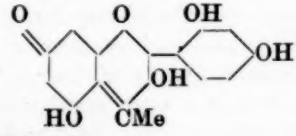
The same effect in the phenyl nucleus can be seen by comparing the last-mentioned dye with the following:

(5) 

Violet with potassium hydroxide, mauve dyeings on alum, blue-black dyeings on chrome.

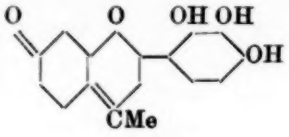
(6) 

Blue with potassium hydroxide, violet dyeings on alum and chrome.

(7) 

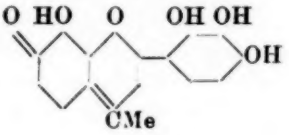
Crimson with potassium hydroxide, maroon on chrome.

The following comparisons show the tendency of three hydroxyl groups in the 1:2:3-position to produce a brown colour. Compare (1) with:

(8) 

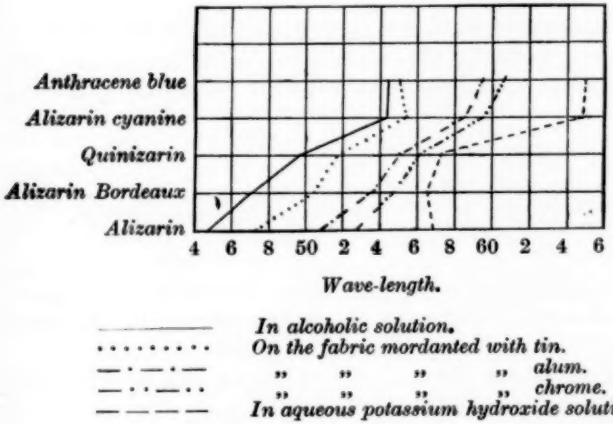
Brownish-red with potassium hydroxide, dyeings are no deeper than those given by (1).

and compare (2) with:

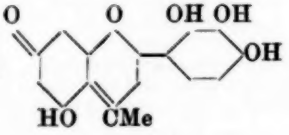
(9) 

Violet-red with potassium hydroxide, dyeing on chrome is brown similar to that given by anthragallol.

FIG. 11.



The favourable effect of the *o*-grouping in the benzo-nucleus is eclipsed by the effect of the 1:2:3-grouping in the phenyl group. Compare (5) with:

(10) 

Dark-red with potassium hydroxide.

In Fig. 11 the wave-length of the centre of the absorption band or group of bands has been plotted for the various dyes under different conditions. The points corresponding with similar conditions have been joined, with the result that a very regular shift of the centre of the absorption band towards the red has been

observed as we pass from alizarin to alizarin-Bordeaux, quinizarin, alizarin-cyanine, and anthracene-blue. This shift is shown equally well in the five different conditions, namely, (1) in alcoholic solution, (2) with potassium hydroxide, (3) on tin, (4) on alumina, and (5) on chrome. Whether any weight should be laid on a result obtained by taking the mean of a group of bands is a matter for further consideration. Purpurin is somewhat anomalous. Increasing the electropositive character of the combined radicle produces much less shift of the band in purpurin than in the other dyes of this series. It is hoped to give later some account of the shift of bands due to addition of hydroxyl groups, on the hypothesis that the tension in an oscillating chain of double and single bands depends also on the modification of the electric field in the molecule by these hydroxyl groups.

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[*Received, April 6th*, 1916.]

XLIII.—*A Space Formula for Benzene. Part II.*

By JOHN NORMAN COLLIE.

NEARLY twenty years ago the author published Part I. of this paper (T., 1897, **71**, 1013). This communication deals with a continuation of Part I., and shows how the molecules of benzene might be expected to pack together in the solid form of crystalline benzene.

An essential part of the space formula for benzene advocated by the author was its dynamic nature; Kekulé fully recognised the importance of a system in vibration as the best representation of the benzene molecule, and even now, fifty years later, Kekulé's formula for benzene (with very slight alteration) remains the best.

Any advances in representation of the benzene molecule must be made along the lines laid down by Kekulé.

That the benzene molecule is in a state of continual vibration must be recognised; moreover, it has this in its favour: it precludes any possibility of the existence of enantiomorphous benzene substitution products, and avoids the difficulties met with in those space formulæ for benzene where all the carbon atoms are not in the same plane.

The space formula advocated by the author differs in one respect from other formulæ: it can easily be modified to suit various

demands; it is perfectly in line with the formulæ suggested by Kekulé, Baeyer, Ladenburg, Claus, etc.

In building up the space formula for benzene only three assumptions were made use of:

(1) Symmetry of the carbon and hydrogen atoms about the centre of the molecule.

(2) The tetrahedral environment of every carbon atom.

By tetrahedral environment it is assumed that if the carbon atom is a sphere, and that when four other atoms are united to it, they will take up positions represented by the corners of a tetrahedron circumscribed about the sphere, or as near those positions as possible. This can be seen in every carbon atom in Bragg's model of the diamond (W. H. and W. L. Bragg, "*X*-Rays and Crystal Structure," p. 106).

(3) Movement of the carbon atoms about the centre of gravity of the mass, or rotational movement about their own centres; also movement of the hydrogen atoms about the carbon atoms to which they are attached.

FIG. 1.

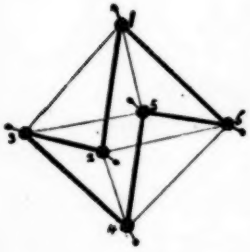


Fig. 1 shows how the carbon and hydrogen atoms are supposed to be arranged. The thick lines represent how the carbon atoms are united to one another.

Fig. 2, *A*, shows, by means of dotted lines, how the carbon atoms might move or swing about the centre of gravity of the mass of the molecule. *B* shows the middle phase of such a movement; all the carbon atoms are on one plane. It represents the centric formula for benzene. *C* shows the end of the swing.*

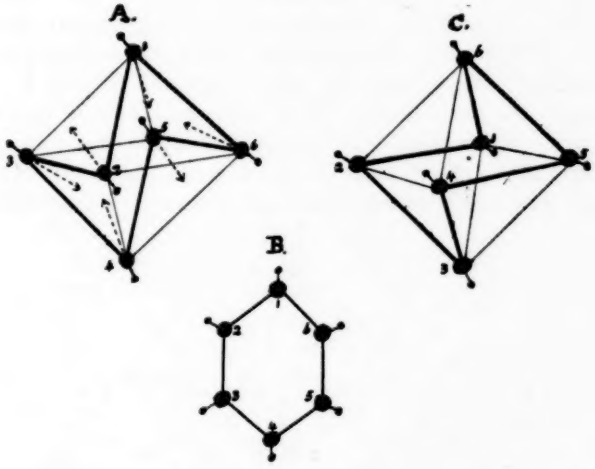
In the swing from *A* to *C*, before the phase *B* is reached, the carbon atom 1 moves towards 2 or 6; in doing so, if it slightly turns on its axis, and the carbon atoms 2 or 6 do the same, at some point intermediate between phase *A* and *B*, there will be an approach to what is recognised as a double binding, for the unoccupied fourth point of attraction on 1 will be turned towards the same points on 2 or 6. If this state of affairs happens between 1 and 2, then the same thing will happen between 3 and 4 and 5 and 6. When it has reached phase *B* carbon atom 1 will again have taken up its normal position between 2 and 6, and will pass on to phase *C*. Owing, however, to the disturbance introduced on its journey from phase *A* to *B*, a swing will have been given to it. Its path will be that of a figure of eight, and so on the return

* In Fig. 2 *A*, the carbon atom 2 is in the front of the octahedron, in *C* the carbon atom 1 is in the front of the octahedron.

swing from *C* to *A* the approach to a double binding will be between 1 and 6, 2 and 3, and 4 and 5. These two phases will represent the two Kekulé phases for benzene.

Another fact might be pointed out, namely, that during the swing from phase *A* to phase *C*, carbon atom 1 is travelling towards carbon atoms 2, 4, and 6; these are the two ortho- and the para-carbon atoms; it does not approach either carbon atoms 3 or 5, the meta-ones. This might afford an explanation of production of ortho- and para-compounds at the same time, but no meta-derivative. It would also be in harmony with the idea that in the production of ortho- and para-compounds the entering group first becomes attached to the atom united to the benzene nucleus (com-

FIG. 2.



pare the production of *o*- and *p*-chloroacetanilide from *N*-chloroacetanilide, $C_6H_5{\cdot}NHCl{\cdot}CO{\cdot}CH_3$), and that meta-compounds are produced when the entering group is first associated with an atom that is next but one to the benzene nucleus.

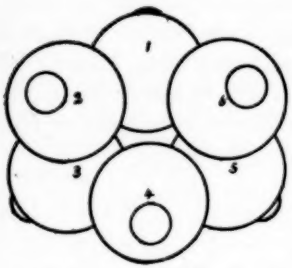
In Figs. 1 and 2 the carbon atoms are apparently shown some distance apart from one another, but the black circles are merely meant to show the centre of the spheres of influence of the carbon atoms, and Fig. 3 could be equally said to represent the molecule of benzene. The large circles represent the carbon atoms, the small ones the hydrogen atoms.

Recently Prof. W. H. Bragg and Mr. W. L. Bragg have proved by means of physical measurements that in certain crystals the atoms are arranged in a definite manner. It is worth while seeing

whether, after having built up a space formula for benzene, a reasonable association of such benzene molecules could be made to occupy a lattice representing the crystal of benzene.

There are many ways in which octahedra representing the benzene molecule can be fitted together, but there seems to be only *one* way that will give a perfectly symmetrical arrangement.

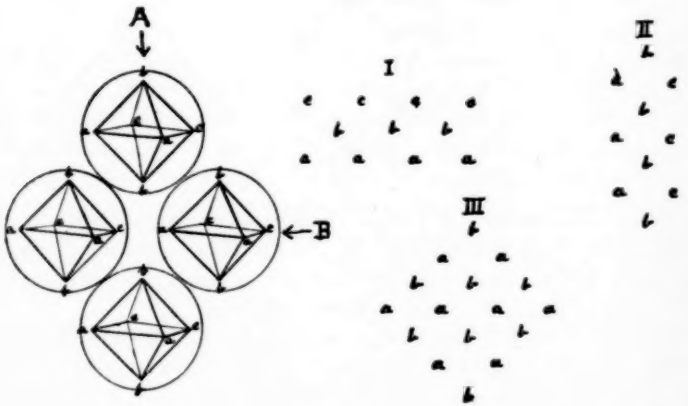
Fig. 3.



In Fig. 4 the four circles represent four benzene molecules. If one looks down in the direction *A*, the arrangement I is seen; in the direction *B*, II is seen, whilst in a direction at right angles to *A* and *B*, III is seen.

If the middle plane opposite *B* at right angles to the plane of the paper is taken, containing four (*a*) carbon atoms and four (*c*) carbon atoms it can be represented as a series of squares with carbon atoms at the four corners, Fig. 5, I. But this represents the arrangement of the carbon atoms if benzene molecules are represented by regular octahedra, as in Fig. 2, *A* and *C*. That such is the case is unlikely; it is more probable that some intermediate phase would be more stable than

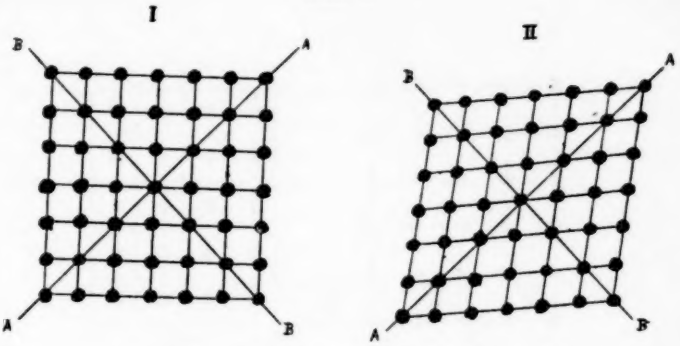
Fig. 4.



the two extreme ones, and for these reasons: (1) the four points of attraction on the carbon atoms are not directed out from a point in directions represented by lines drawn from the centre of a regular tetrahedron to its corners, although they are not far from it. (2) The fourth unsaturated point of attraction on each

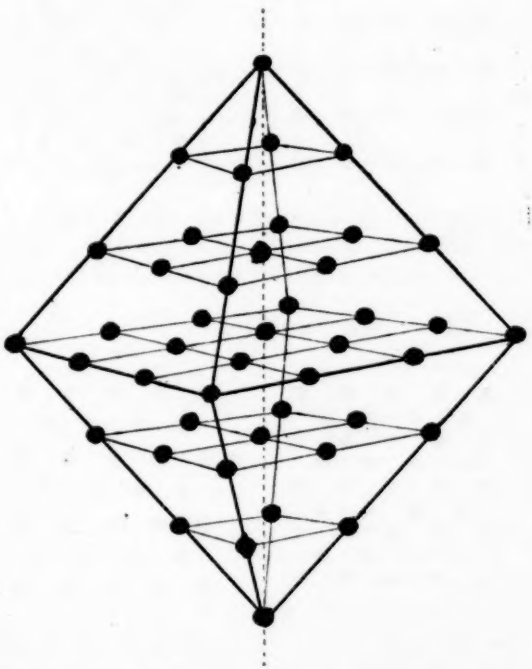
carbon atom, although it points inwards, does not point to the centre of the benzene nucleus.

FIG. 5.



These forces would certainly tend to produce an intermediate phase, and at the same time the hydrogen atoms would approach

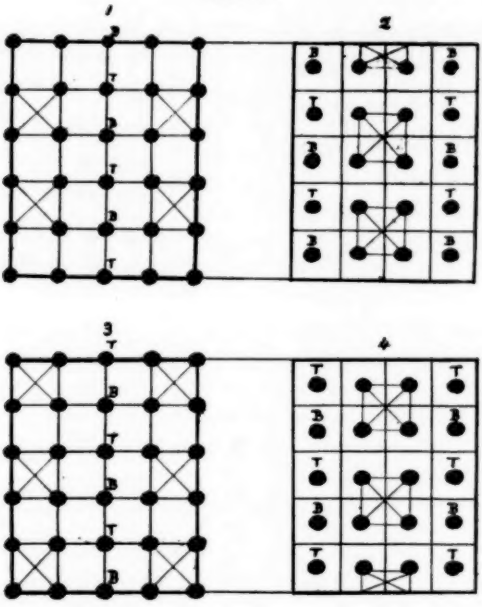
FIG. 6.



together in two sets of three, at the two opposite sides of the molecule. This can be seen in Fig. 2, *A*. As the carbon atoms

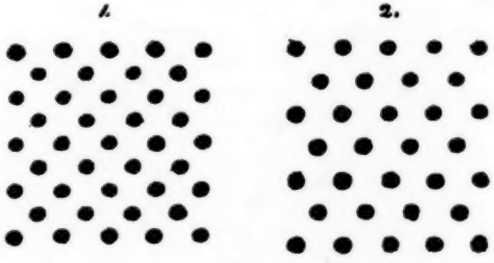
2, 4, and 6 rotated slightly inwards, the three hydrogen atoms would approach one another, and the hydrogen atoms on carbon atoms 1, 3, and 5 would do the same on the other side of the molecule.

FIG. 7.



A slight distortion of the molecule would result. Either the axes of the molecule would become tilted, or they might be elongated or shortened; the latter hypothesis is the more probable.

FIG. 8.



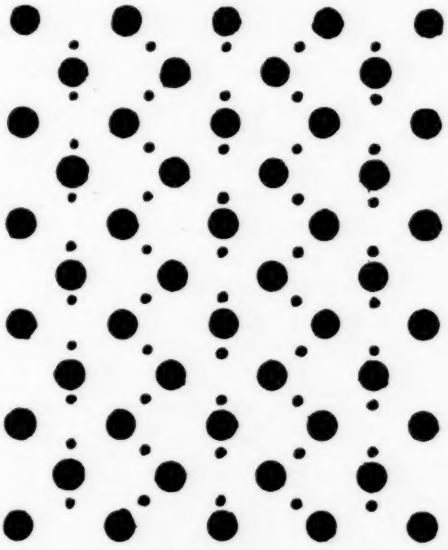
Also as benzene crystallises in the orthorhombic system, the first hypothesis is untenable. Fig. 5, II, shows what would occur if the assemblage of carbon atoms in I were pulled out along the axis A, A.

Fig. 6 shows what would happen to a regular octahedral lattice (built up of octahedra in the manner shown in Fig. 4) if it were pulled out along the axis A.

The axial ratios of the regular octahedral lattice are 1:1:1. The axial ratios in Fig. 6 are 0·893:1:0·786.

This result has been obtained by pulling out the axis A, A to 1·12. By doing this, axis B, B becomes 0·88; the third axis remains 1. The axial ratios of a benzene crystal are 0·891:1:0·799. Of course, by pulling out the axis A, A a greater or less amount than to 1·12 other results would be obtained; for instance, by pulling it out to 1·1 the axial ratios would be 0·909:1:0·818, or by pulling it out

FIG. 9.



to 1·15 the axial ratios would be 0·869:1:0·739. The way in which the octahedra are piled together in such a space lattice (Fig. 4) can be seen in Fig. 7, where successive layers are taken. A crossed square represents the four carbon atoms on a plane through the middle of an octahedron, the a and c carbon atoms in Fig. 4; T represents the carbon atom at the top of an octahedron, B represents the carbon atom at the bottom of an octahedron. It will be seen, therefore, that in Fig. 7, 1, if a bottom carbon atom is taken, in 2, at the same place will be the four carbon atoms of the centre of the octahedron, in 3, at the same place will be found a top carbon atom, and in 4 will be found a space, after which row 5 would be exactly the same as row 1.

Fig. 8, 1, shows what is seen when looking along any of the

three axes; 2 what is seen when looking between two carbon atoms towards the middle of any octahedron.

If the hydrogen atoms are arranged symmetrically as shown in Fig. 1, then on looking along any one of the axes of the octahedra in the space lattice Fig. 4 the arrangement in Fig. 9 will be seen; the large dots are the carbon atoms, the small dots represent the hydrogen atoms.

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XLIV.—3-*Phenanthrol*-4-*aldehyde.**

By the late JOHN WALTER SMITH.

WITH a view to the synthesis of pyrone derivatives derived from phenanthrene, which may be expected to possess in a high degree the power of forming blue additive compounds with iodine (compare Barger and Starling, T., 1915, **107**, 411), the preparation of a hydroxyaldehyde of phenanthrene was undertaken. From the exhaustive experiments of Werner and his pupils (*Annalen*, 1902, **321**, 248), 3-phenanthrol appeared to be the most readily accessible phenol in this series, and it was accordingly selected as a starting point. It was subjected to the action of hydrogen cyanide by Gattermann's method, and an hydroxyaldehyde was obtained in good yield. In this reaction the aldehyde group enters into the para-position, but when this position is not accessible, as in the present case, an ortho-hydroxyaldehyde is formed. That such is indeed the nature of the present reaction product is probable from the fact that it gives an intense (green) coloration with ferric chloride, and is rendered certain by the production of a coumarin on heating with acetic anhydride and sodium acetate. This means that the aldehyde must have either of the following constitutions:

(I.)

or

(II.)

* The preparation of this, the first aldehyde of the phenanthrene series, was undertaken by Mr. Smith at my suggestion, when he was a student at Goldsmiths' College. His participation in the work, which he afterwards continued at the West Ham Municipal Technical Institute, came to an untimely end by his death in 1915. I have recently been able to determine the constitution of the aldehyde by conversion into morphol and have therefore prepared the present note for publication.—G. BARGER.

It has been possible to convert the aldehyde almost quantitatively into 3:4-dihydroxyphenanthrene (morphol) so that the substance has the constitution I. An account of this and further experiments will be published later.

Experimental.

The necessary 3-phenanthrol was prepared according to Werner, whose directions were found to be thoroughly satisfactory. The phenanthrene employed was a very pure specimen (from the Gesellschaft für Teerverwertung, Duisburg). The yield of potassium phenanthrene-3-sulphonate given by Werner, namely, 31 grams from 100 grams of phenanthrene, was easily obtained and occasionally rose to 40 grams. It was found advisable to boil the barium precipitate with even larger quantities of water than those employed by Werner. The fusion with potassium hydroxide proceeded exactly as Werner indicates, and the yield of the crude precipitated phenanthrol was almost a theoretical one. On the large scale this product was most readily purified by distilling in a Claisen flask, with condenser fused on, under a pressure of 2 mm. The distillate melted at 117°, and in this way 111·5 grams were obtained from 119 grams of the crude product, so that the latter was almost pure.

For the conversion into the aldehyde, 10 grams of the phenol were dissolved in 50 c.c. of dry benzene; 12 grams of aluminium chloride and 14 c.c. of hydrogen cyanide were added, and hydrogen chloride was passed in for one hour at 0°. The mixture was then raised for one to two hours to 45°. The contents of the flask were washed out with ether, mixed with ice, boiled with water for three hours to decompose the imino-compound, extracted with benzene, dried, and distilled. The yield amounts to 70 per cent. of the theoretical. In one experiment with zinc chloride, instead of aluminium chloride, the yield was only 10 per cent.

3-Phenanthrol-4-aldehyde was the only product which could be isolated, in addition to small quantities of unchanged phenol. The substance need not necessarily be distilled, and crystallises from absolute or 90 per cent. alcohol in pale brown crystals. On recrystallisation from light petroleum or ether and light petroleum the aldehyde forms slender, lemon-yellow needles melting at 98° and boiling at 163—165° in the vacuum of a Gaede pump and at about 170° under a pressure of 2 mm.:

0·1520 gave 0·4506 CO_2 and 0·0662 H_2O. C = 80·9; H = 4·8.

$C_{15}H_{10}O_2$ requires C = 81·1; H = 4·5 per cent.

The substance is scarcely soluble in boiling water, very readily

so in hot alcohol, much less in cold alcohol, very readily in benzene or ether, and only sparingly so in light petroleum. It is soluble in ammonia and in sodium carbonate, more readily so in sodium hydroxide; the sodium salt is only sparingly soluble in water. In alcoholic solution the aldehyde gives an intense green coloration with ferric chloride, resembling that of catechol. The solution in concentrated sulphuric acid is blood red.

No additive compound with sodium hydrogen sulphide was obtainable, but condensation products with primary amines are available for the isolation of the aldehyde.

3-*Hydroxyphenanthrylideneaniline* is formed by heating the constituents in alcoholic solution. It separates from alcohol in orange-yellow crystals melting at 117—118°. The yield is 85 per cent.:

0·2148 gave 9·4 c.c. N_2 at 17° and 756 mm. N = 5·0.

$C_{21}H_{15}ON$ requires N = 4·7 per cent.

This substance gives with ferric chloride the same coloration as the parent substance.

The phenanthrene employed was purchased out of a grant from the Research Fund of the Chemical Society, hereby gratefully acknowledged.

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XLV.—o-*Chlorobenzyl Bromide and its Products of Hydrolysis.*

By ALFRED GODFREY GORDON LEONARD.

THE author has prepared *o-chlorobenzyl bromide* by brominating *o*-chlorotoluene at its boiling point. The product, on treatment with a solution of potassium hydroxide in water and alcohol, gave in varying quantities *o*-chlorobenzyl alcohol, *di-o-chlorobenzyl ether*, and *o*-chlorobenzyl ethyl ether.

EXPERIMENTAL.

o-Chlorobenzyl Bromide, $C_6H_4Cl\cdot CH_2Br$.—*o*-Chlorotoluene was heated to boiling in a flask fitted with a reflux condenser, and the calculated quantity of bromine added in drops by means of a funnel drawn out to a capillary tube. It is advisable to add a few pieces of fireclay to prevent bumping, and to dispense with all cork connexions.

The product was washed with sodium carbonate, dissolved in ether, the solution dried, the ether evaporated, and the residue distilled in a vacuum. It is a colourless liquid boiling at 120°/10 mm., and possesses a peculiar, pungent odour. Its vapour irritates the eyes most powerfully:

0·2414 gave 0·3616 CO_2 and 0·0644 H_2O. C = 40·85; H = 2·96.
0·2404 „ 0·1666 AgCl „ 0·2221 AgBr. Cl = 17·14; Br = 39·31.
C_7H_6ClBr requires C = 40·89; H = 2·94; Cl = 17·26; Br = 38·90 per cent.

Action of Potassium Hydroxide in Aqueous Alcohol on o-Chlorobenzyl Bromide.

o-Chlorobenzyl bromide was heated under reflux with an excess of potassium hydroxide dissolved in water mixed with a small quantity of ethyl alcohol. After six or seven hours the liquid was found to be free from *o*-chlorobenzyl bromide by the absence of any irritating effect on the eyes. The product was then distilled in a current of steam with the following result.

The first product of the steam distillation consisted of oily drops which did not crystallise. The oil was extracted with ether and distilled in a vacuum. It is colourless, and possesses a faint but not unpleasant aromatic odour. Analysis showed it to consist of *o*-chlorobenzyl ethyl ether, $C_9H_{11}OCl$. It distils at 216°/761 mm. or at 103°/8 mm. (Mettler, *Ber.*, 1904, **37**, 3693, gives 212°).

After the distillation in steam had continued for some time the distillate commenced to crystallise in the condenser, when the receiver was changed and the distillation continued. The crystals were collected and were proved by analysis to consist of *o*-chlorobenzyl alcohol, C_7H_7OCl, melting at 70—71° (Mettler, *loc. cit.*, gives 72°).

Di-o-chlorobenzyl Ether, $C_6H_4Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$.—The contents of the flask on cooling after the steam distillation showed the presence of a crystalline residue. This was dissolved in ether, the ether evaporated, and the product twice crystallised from alcohol, from which it separates in colourless, hexagonal prisms melting at 48—49°:

0·3430 gave 0·8302 CO_2 and 0·1432 H_2O. C = 63·03; H = 4·63.
0·1244 „ 0·1333 AgCl. Cl = 26·5.
$C_{14}H_{12}OCl_2$ requires C = 62·92; H = 4·53; Cl = 26·56 per cent.

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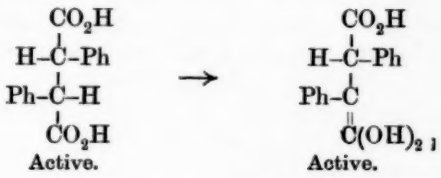
XLVI.—*Studies in the Phenylsuccinic Acid Series Part III. The Optically Active Phenylsuccinic Acids and their Derivatives.*

By Henry Wren and Howell Williams.

In previous communications (Wren and Still, T., 1915, **107**, 444, 1449) the resolution of *r*-diphenylsuccinic acid into its optical antipodes has been described, and the properties of several derivatives of the optically active acids have been discussed. It was observed that *d*-diphenylsuccinic acid is not appreciably racemised by prolonged treatment with an excess of aqueous potassium hydroxide at the temperature of boiling water. This result was unexpected since it has been generally observed that optically active acids which have a hydrogen atom attached to the asymmetric carbon atom in the α-position with respect to the carboxyl group readily undergo more or less complete racemisation under these conditions (compare Rothe, *Ber.*, 1914, **47**, 843; McKenzie and Widdows, T., 1915, **107**, 702), and, in consequence, this particular type of racemisation has been attributed to desmotropic change with the concomitant disappearance of molecular asymmetry.*. Probably, in the diphenylsuccinic acids, the mobility of the hydrogen atoms is considerably restricted by the proximity of groups of rather high molecular weight (compare Meyer, *Annalen*, 1888, **250**, 124), and the tendency to pass into the desmotropic form is thus lessened, but this explanation is not readily reconcilable with the observation of McKenzie and Widdows (*loc. cit.*) that the not very dissimilarly constituted *d*-phenyl-*p*-tolylacetic acid undergoes extensive racemisation under comparatively less drastic conditions. An alternative hypothesis appeared to present itself, based on the fact that two asymmetric carbon atoms are present in the diphenylsuccinic acids. In such cases, the evidence obtained during the study of racemisation points to the conclusion that one asymmetric carbon atom is first affected; thus, Winther (*Zeitsch. physikal. Chem.*, 1905, **56**, 466, 720) showed that *d*-tartaric acid is transformed in the presence of alkali into mesotartaric acid, which is subsequently partly converted into the racemic form, a condition of equilibrium being finally established between the two latter. Similarly, Wren and Still (*loc. cit.*) isolated mesodiphenylsuccinic acid from the partly racemised product obtained by the hydrolysis of ethyl *d*-diphenylsuccinate with aqueous alcoholic potassium hydroxide

* A review of the literature on this subject may be found in the paper of McKenzie and Widdows (*loc. cit.*).

solution. If, now, the occurrence of desmotropism be considered as the cause of racemisation, the change shown in the annexed scheme may be assumed to take place in the case of the active diphenylsuccinic acids:



Owing to the presence of the second asymmetric carbon atom, the activity of the product does not vanish as a result of desmotropic change; the regeneration of the acid, therefore, occurs under asymmetric conditions which might conceivably lead, in part, to a regeneration of the active form, and thus to an apparently enhanced stability of the active acid. To test this point, it was decided to prepare an optically active acid as closely similar as possible to diphenylsuccinic acid, but containing only one asymmetric carbon atom; for this purpose, phenylsuccinic acid was chosen.

r-Phenylsuccinic acid is readily resolved into its active components by the fractional crystallisation of the brucine salts from ethyl-alcoholic solution, in which the brucine salt of the *d*-acid is the more sparingly soluble. d-*Phenylsuccinic acid* crystallises from water in granular aggregates or long, well-defined prisms; both forms appear to be perfectly stable when dry, but, on one occasion, the acid was observed to separate from its aqueous solution in long prisms which, after remaining overnight in contact with the solution, were almost completely converted into the granular variety. It melts at 173—174° after previous softening, and has $[\alpha]_D^{15\cdot4}$ +173·4° when dissolved in acetone. l-*Phenylsuccinic acid*, like its optical antipode, melts at 173—174° after previous softening, and has $[\alpha]_{1D}^{4}$ −173·3° in acetone solution. *r*-Phenylsuccinic acid melts at 168° (Higson and Thorpe, T., 1906, **89**, 1472). As in the case of the diphenylsuccinic acids, however, the observed melting point is to some extent dependent on the mode of heating and the diameter of the capillary tube employed. Although visible decomposition does not appear to occur, the acids are not completely stable at their melting points and, by slightly prolonging the duration of heating at this temperature it can readily be shown that partial conversion into the anhydride takes place and, further, that the latter and the residual acid are practically completely racemised.

Methyl and *ethyl* d-*diphenylsuccinates*, as well as d- and l-*phenyl-*

succinic anhydrides, have been prepared, and their properties investigated.

Under the action of alkali the behaviour of the active phenylsuccinic acids and their derivatives is remarkably similar to that of the active diphenylsuccinic acids and their compounds. Thus *d*-phenylsuccinic acid, like *d*-diphenylsuccinic acid, is scarcely affected by prolonged treatment with an excess of aqueous alkali at the temperature of boiling water, whilst, as in the case of the corresponding diphenylsuccinic derivative, considerable racemisation is observed during the hydrolysis of methyl *d*-phenylsuccinate by aqueous alcoholic potassium hydroxide solution. At a higher temperature, however, *d*-phenylsuccinic acid is almost completely racemised when heated in the presence of an excess of aqueous alkali. Nevertheless, this result appears to be due to the comparatively high temperature employed, since a very similar effect is observed when the alkali is replaced by water.

The conversion of *d*-phenylsuccinic anhydride into the acid by means of hot water is accompanied by slight racemisation, the behaviour thus resembling that of the active diphenylsuccinic anhydrides.

A comparison of the melting points of the similar active and racemic compounds in the two series shows that the active acids and anhydrides have higher melting points than the corresponding racemic substances, whilst the reverse is the case with the methyl esters. The ethyl esters of the phenylsuccinic acids have not been obtained in the solid condition.

The specific rotations of the active phenylsuccinic acids and their derivatives are uniformly much lower than those of the diphenylsuccinic acids and their compounds. In each series, however, the activity of the free acid is somewhat greater than that of the methyl ester and considerably in excess of that of the ethyl ester, whilst, also, the anhydrides are less active than the acids. Further, if in the two series the specific rotations of similar compounds in different solvents are arranged in order of magnitude, it will be noticed that this order is the same in each instance in the cases of the acids and methyl esters, but not with the ethyl esters or the anhydrides.

Experimental.

Resolution of r-*Phenylsuccinic Acid by Brucine in Ethyl-alcoholic Solution.*

A mixture of *r*-phenylsuccinic acid (30 grams) and brucine (144 grams) was dissolved by gentle warming in rectified spirit (2400 c.c.). The filtered solution was allowed to cool to the tem-

perature of the laboratory with frequent stirring, when a voluminous, white, crystalline precipitate separated. After remaining for three hours at 15° the crop was filtered and dried, when 106 grams of product were obtained which was purified by repeated crystallisation from rectified spirit, 20 c.c. of the solvent being used for each gram of salt. The course of the resolution was followed by determining the specific rotation of the acid recovered from the successive filtrates. The following values for $[\alpha]_D$ were thus obtained, the observations being made in acetone solution: $-102{\cdot}5°$, $-43{\cdot}5°$, $+40{\cdot}9°$, $+102{\cdot}2°$. The crop from which the last filtrate had been obtained, which consisted of indistinct crystals weighing 40·5 grams, was decomposed by treatment with dilute hydrochloric acid and extracted with ether, whereby 6·7 grams of *d*-phenylsuccinic acid, having $[\alpha]_D$ $+168{\cdot}0°$ in acetone solution, were isolated. After two crystallisations of this acid from water in the proportion of 50 c.c. of solvent to each gram of acid, this value had increased to $+173{\cdot}4°$ and then remained unchanged after a further crystallisation.

α-Phenylsuccinic acid separates from water in granular aggregates or well-defined prisms. It is readily soluble in the hot solvent, very sparingly so in the cold. It dissolves freely in cold acetone or ether, less readily in cold methyl and ethyl alcohols, very sparingly in boiling benzene. When rapidly heated in a capillary tube it melts at 173—174° after softening from 171°, and without suffering visible decomposition; if the molten mass is allowed to solidify, however, and the solid again heated, an indefinite melting point, 130—155°, is observed. Analyses and determinations of specific rotation were made with samples which had been dried in a vacuum over calcium chloride until constant in weight:

0·1566 gave 0·3562 CO_2 and 0·0736 H_2O. C = 62·0; H = 5·3.

$C_{10}H_{10}O_4$ requires C = 61·8; H = 5·2 per cent.

The following determinations of the specific rotation were made:
In acetone solution:

$l = 2$, $c = 1{\cdot}8025$, $\alpha_D^{15{\cdot}4} + 6{\cdot}25°$, $[\alpha]_D^{15{\cdot}4} + 173{\cdot}4°$.
$l = 2$, $c = 1{\cdot}8235$, $\alpha_D^{16} + 6{\cdot}32°$, $[\alpha]_D^{16} + 173{\cdot}3°$.

In ethyl-alcoholic solution:

$l = 2$, $c = 1{\cdot}5340$, $\alpha_D^{16{\cdot}5} + 4{\cdot}55°$, $[\alpha]_D^{16{\cdot}5} + 148{\cdot}3°$.

In ethyl acetate solution:

$= 2$, $c = 1{\cdot}5500$, $\alpha_D^{15{\cdot}5} + 5{\cdot}40°$, $[\alpha]_D^{15{\cdot}5} + 174{\cdot}2°$.

Preparation of l-Phenylsuccinic Acid.

The isolation of *l*-phenylsuccinic acid was effected by fractional crystallisation from water of the crude lævorotatory mixture of

acids obtained from the filtrate from the first crop of brucine salt (see above). In one experiment, crude *l*-phenylsuccinic acid (9·7 grams, $[\alpha]_D - 102·5°$ in acetone solution) was dissolved in boiling water (600 c.c.). A granular, crystalline crop separated on cooling which, after being dried, weighed 3·8 grams and had $[\alpha]_D - 168·4°$ when dissolved in acetone. After two further crystallisations from water (60 c.c. of solvent being used for each gram of acid) this value had increased to $-173·3°$, which agrees well with the constant specific rotation determined for the *d*-acid.

l-*Phenylsuccinic acid* closely resembles its *d*-isomeride in appearance and properties. When heated in a capillary tube it melts at 173—174°, after marked softening at 171°; when the molten mass is allowed to solidify and again heated, an indefinite melting point is observed:

0·1548 gave 0·3510 CO_2 and 0·0725 H_2O. C = 61·8; H = 5·2.

$C_{10}H_{10}O_4$ requires C = 61·8; H = 5·2 per cent.

The specific rotation was determined in acetone and in methyl-alcoholic solution:

In acetone solution:

$$l = 2,\ c = 1·4830,\ a_D^{14·5} - 5·14°,\ [\alpha]_D^{14·5} - 173·3°.$$

In methyl-alcoholic solution:

$$l = 2,\ c = 1·9415,\ a_D^{12·5} - 5\ 71°,\ [\alpha]_D^{12·5} - 147·1°.$$

Attempts to Resolve r-*Phenylsuccinic Acid by means of Brucine in Aqueous Solution.*

In the preliminary portion of the investigation a considerable number of attempts were made to effect the resolution of *r*-phenylsuccinic acid by brucine in aqueous solution. With small quantities of material these experiments appeared to proceed successfully, the brucine salt of the *l*-acid being the more sparingly soluble. Thus, in one instance, *r*-phenylsuccinic acid (3 grams) and brucine (14·4 grams) were dissolved in hot water (210 c.c.). The solution was allowed to remain in an ice-chest for two days, when a crop of well-defined, rhombic crystals separated which weighed 11·7 grams. These were twice crystallised from water (14 c.c. per gram of salt). The final crop so obtained weighed 5·8 grams and, after decomposition with dilute hydrochloric acid and extraction with ether, yielded impure *l*-phenylsuccinic acid which had $[\alpha]_D - 131·6°$ in acetone solution. The acids extracted from the successive filtrates had $[\alpha]_D + 86·8°$, $+47·6°$, and $+10·5°$ respectively when dissolved in acetone. When, however, attempts were made to repeat the experiment on a larger scale, using ten times the above quantities of material, very irregular results were

obtained. Apparently, the brucine salt suffers considerable hydrolysis since, at times, the crops appeared to be contaminated with free brucine. As the resolution was found to proceed normally in alcoholic solution, these experiments were not further continued.

Action of Heat and Alkali on the Optically Active Phenylsuccinic Acids.

With the object of investigating the change which the active phenylsuccinic acids suffer at their melting point, *d*-phenylsuccinic acid (0·3411 gram) was heated during ten minutes at 168—172°. The loss in weight amounted to 0·0200 gram, equivalent to 5·86 per cent., whilst complete conversion into the anhydride requires a loss of 9·3 per cent. The residue solidified readily when cooled, and was treated with successive small quantities of cold benzene, in which phenylsuccinic anhydride is readily soluble, whereas the acid dissolves very sparingly. On polarimetric examination the residual acid was found to have $[\alpha]_D$ +1·2° in acetone solution, whilst the anhydride gave the value $[\alpha]_D$ +1·66° when dissolved in benzene. After crystallisation from light petroleum (b. p. 40—60°) containing a little benzene, the anhydride melted at 50—52°. For *r*-phenylsuccinic anhydride Dehn and Thorpe (T., 1906, **89**, 1882) gave the value 53—54°.

d-Phenylsuccinic acid is scarcely affected by treatment with an excess of aqueous alkali at the temperature of boiling water. In one experiment pure *d*-phenylsuccinic acid (0·5 gram) was dissolved in aqueous potassium hydroxide solution (0·866*N*, 25 c.c.), the quantity of alkali being about four times that necessary for neutralisation. A portion of this solution, when examined in a 2-dcm. tube immediately after preparation, had α_D +3·16°. The solution was heated during four hours on the boiling-water bath; at the end of this period the solution was cooled and a portion of it examined in a 2-dcm. tube, when the value α_D +3·09° was observed. The recovered acid had $[\alpha]_D$ +167·4° in acetone solution ($l=2$, $c=2·2635$, α_D +7·58°).

Similar experiments were performed at a somewhat higher temperature, when almost complete racemisation was found to occur. In one instance, pure *d*-phenylsuccinic acid (0·3548 gram) was heated with 10 c.c. of aqueous potassium hydroxide solution (1·17*N*) during two hours at 150°. The resulting solution was very feebly dextrorotatory, whilst the recovered acid had $[\alpha]_D$ +9·6° in acetone solution. Racemisation, however, seems to be attributable to the high temperature used, rather than to a specific action of the alkali hydroxide, since a very similar result was obtained when *d*-phenylsuccinic acid (0·35 gram) was heated with water (10 c.c.) for two

hours at 152°; in this case, the recovered acid had $[\alpha]_D + 23{\cdot}6°$ when dissolved in acetone.

Esterification of the Phenylsuccinic Acids with Methyl and Ethyl Alcohols.

The phenylsuccinic acids are readily converted into the dimethyl esters by the action of methyl alcohol and concentrated sulphuric acid according to the Fischer-Speier method, the yields being satisfactory.

Methyl d-*phenylsuccinate* is a colourless, slightly viscous liquid which completely solidifies in a freezing mixture of ice and salt. It boils at 161—162°/16 mm.:

0·1652 gave 0·3894 CO_2 and 0·0950 H_2O. C = 64·3; H = 6·4.
0·1698 „ 0·4036 CO_2. C = 64·8.
$C_{12}H_{14}O_4$ requires C = 64·8; H = 6·4 per cent.

The specific rotation was determined in a number of solvents:

In acetone solution:

$$l = 2,\ c = 1{\cdot}7235,\ \alpha_D^{19} + 4{\cdot}90°,\ [\alpha]_D^{19} + 142{\cdot}2°.$$

In benzene solution:

$$l = 2,\ c = 1{\cdot}4430,\ \alpha_D^{15} + 4{\cdot}59°,\ [\alpha]_D^{15} + 159{\cdot}0°.$$

In carbon tetrachloride solution:

$$l = 2,\ c = 1{\cdot}2720,\ \alpha_D^{15} + 4{\cdot}32°,\ [\alpha]_D^{15} + 169{\cdot}8°.$$

In ethyl-alcoholic solution:

$$l = 2,\ c = 1{\cdot}5580,\ \alpha_D^{12} + 4{\cdot}39°,\ [\alpha]_D^{12} + 140\ 9°.$$

In ethyl acetate solution:

$$l = 2,\ c = 1{\cdot}2670,\ \alpha_D^{11{\cdot}5} + 3{\cdot}82°,\ [\alpha]_D^{11{\cdot}5} + 150{\cdot}7°.$$

Methyl r-*phenylsuccinate* separates from boiling light petroleum (b. p. 40—60°), in which it is sparingly soluble in well-defined clusters of prisms. It is freely soluble in cold benzene, chloroform, carbon tetrachloride, ether, or acetone, less readily so in cold methyl or ethyl alcohol. It melts at 57·5—58·5°:

0·1359 gave 0·3214 CO_2 and 0·0796 H_2O. C = 64·5; H = 6·6.
$C_{12}H_{14}O_4$ requires C = 64·8; H = 6·4 per cent.

0·5066 required for hydrolysis 9·2 c.c. of alcoholic potassium hydroxide solution (0·494*N*). Calc., 9·23 c.c.

Esterification of the phenylsuccinic acids by ethyl alcohol is conveniently effected by treatment with 3 per cent. ethyl-alcoholic hydrogen chloride. The acid was heated with this solution at its boiling point during three hours, the bulk of the alcohol removed by distillation, and the residue heated for a further period of three

hours with a fresh portion of solution. After purification in the usual manner, good yields of the respective esters were obtained.

Ethyl d-*phenylsuccinate* is a colourless oil which does not solidify in a freezing mixture of ice and salt. It boils at 166°/13 mm.:

0·1703 gave 0·4197 CO_2 and 0·1104 H_2O: C = 67·2; H = 7·3.
$C_{14}H_{18}O_4$ requires C = 67·2; H = 7·2 per cent.

The following determinations of the specific rotation were made:

In acetone solution:

$$l = 2,\ c = 3{\cdot}0905\ ;\ \alpha_D^{13} + 6{\cdot}39°,\ [\alpha]_D^{13} + 103{\cdot}4°.$$

In carbon tetrachloride solution:

$$l = 2,\ c = 1{\cdot}8530,\ \alpha_D^{16} + 4{\cdot}84°,\ [\alpha]_D^{16} + 130{\cdot}6°.$$

In ethyl-alcoholic solution:

$$l = 2,\ c = 2\ 2425,\ \alpha_D^{15{\cdot}5} + 4{\cdot}52°,\ [\alpha]_D^{15{\cdot}5} + 100{\cdot}8°.$$

Ethyl r-*phenylsuccinate* is a colourless, slightly viscous liquid which boils at 160°/10 mm. It does not solidify in a freezing mixture of ice and salt:

0·1858 gave 0·4566 CO_2 and 0·1192 H_2O. C = 67·0; H = 7·2.
$C_{14}H_{18}O_4$ requires C = 67·2; H = 7·2 per cent.

The hydrolysis of the esters of the optically active phenylsuccinic acids by aqueous alcoholic potassium hydroxide is accompanied by considerable racemisation. In one experiment methyl *d*-phenylsuccinate (1 gram) was heated with boiling aqueous alcoholic potassium hydroxide solution (1·123*N*, 50 c.c.) during two hours. The resulting solution was heated in an open dish until the alcohol was expelled, water being added from time to time so that the total volume of solution remained sensibly constant. The cold solution was acidified, and the liberated phenylsuccinic acid repeatedly extracted with ether. Its specific rotation was determined in acetone solution:

$$l = 2,\ c = 2{\cdot}4325,\ \alpha_D + 5{\cdot}36°,\ [\alpha]_D + 110{\cdot}2°.$$

Pure *d*-phenylsuccinic acid has $[\alpha]_D^{15{\cdot}4} + 173{\cdot}4°$ under similar conditions.

The residual acid obtained in the above experiment was re-esterified with methyl alcohol and sulphuric acid; the semi-solid mixture of esters had $[\alpha]_D + 86{\cdot}3°$ ($l = 2$, $c = 2{\cdot}3870$, $\alpha_D + 4{\cdot}12°$) when dissolved in acetone, whilst the original ester had $[\alpha]_D^{19} + 142{\cdot}2°$ in like circumstances. The mixture was spread on porous earthenware, washed with a little light petroleum (b. p. 40—60°), and the residue crystallised from this solvent. Characteristic crystals of methyl *r*-phenylsuccinate were thus obtained which melted at 57·5—58·5° and showed no change in melting point when mixed with the

synthetic racemic ester. In view of the liquid character of methyl *d*-phenylsuccinate and the consequent difficulty of adducing experimental evidence of its optical purity with the small amounts of available material, some such proof of actual racemisation appeared desirable.

Action of Acetyl Chloride on d- *and* l-*Phenylsuccinic Acids.*

Pure *d*-phenylsuccinic acid (3 grams) was cautiously heated with acetyl chloride (10 c.c.). At 40—50° hydrogen chloride was briskly evolved; the temperature was maintained practically constant until the evolution of gas slackened, after which the mixture was gradually heated to its boiling point and kept at this temperature until hydrogen chloride ceased to be evolved. The reaction appeared to proceed in two fairly well-defined stages. The product readily solidified when placed in a desiccator over soda-lime, and was purified by repeated crystallisation from a mixture of benzene (1 vol.) and light petroleum (b. p. 60—80°, 2 vols.) until successive crops had a constant specific rotation.

d-*Phenylsuccinic anhydride* separates from a mixture of benzene and light petroleum in long, colourless needles which melt at 83·5—84·5°. It is readily soluble in cold benzene or chloroform, sparingly so in cold carbon tetrachloride or light petroleum. For analysis and determination of specific rotation it was dried over calcium chloride and paraffin-wax:

0·1586 gave 0·3981 CO_2 and 0·0660 H_2O. C = 68·4; H = 4·7.
$C_{10}H_8O_3$ requires C = 68·2; H = 4·6 per cent.

0·3443, after treatment with water, neutralised 18·85 c.c. 0·205*N*-barium hydroxide solution. Calc., 19·06 c.c.

The following determinations of the specific rotation were made:

In benzene solution:

$l = 2$, $c = 1{\cdot}2985$, $\alpha_D^{15} + 2{\cdot}62°$, $[\alpha]_D^{15} + 100{\cdot}9°$.

$l = 2$, $c = 1{\cdot}2910$, $\alpha_D^{11} + 2{\cdot}60°$, $[\alpha]_D^{11} + 100{\cdot}7°$.

In toluene solution:

$l = 2$, $c = 1{\cdot}5000$, $\alpha_D^{12{\cdot}5} + 3{\cdot}08°$, $[\alpha]_D^{12{\cdot}5} + 102{\cdot}7°$.

In ethyl acetate solution:

$l = 2$, $c = 1{\cdot}0905$, $\alpha_D^{16} + 1{\cdot}98°$, $[\alpha]_D^{16} + 90{\cdot}8°$.

l-*Phenylsuccinic anhydride* was prepared from *l*-phenylsuccinic acid by a process similar to that described for the *d*-isomeride, which it exactly resembles in appearance and properties. It melts at 83·5—84·5°:

0·1402 gave 0·3520 CO_2 and 0·0582 H_2O. C = 68·5; H = 4·7.
$C_{10}H_8O_3$ requires C = 68·2; H = 4·6 per cent.

The specific rotation was determined in benzene and in chloroform solution:

In benzene solution:

$$l = 2,\ c = 1{\cdot}3820,\ a_D^{14} - 2{\cdot}79°,\ [a]_D^{14} - 100{\cdot}9°.$$

In chloroform solution:

$$l = 2,\ c = 0{\cdot}9545,\ a_D^{10{\cdot}5} - 1{\cdot}76°,\ [a]_D^{10{\cdot}5} - 92{\cdot}2°.$$

Action of Water on d-*Phenylsuccinic Anhydride.*—The optically active phenylsuccinic anhydrides appear to be less susceptible to the action of moisture than the corresponding racemic compound. According to Dehn and Thorpe (T., 1906, **89**, 1884), the latter gradually passes into the acid when exposed to the air of the laboratory, the change being almost complete after three weeks; *l*-phenylsuccinic anhydride, on the other hand, when placed in an atmosphere saturated with water-vapour at the temperature of the laboratory, is only slowly converted into the acid, about 60 per cent. of a specimen remaining unchanged at the end of three weeks. On treatment with boiling water, however, hydration readily takes place. In one experiment pure *d*-phenylsuccinic anhydride (0·3443 gram) was heated with water (40 c.c.) on the steam-bath; the oily drops of molten anhydride gradually passed into solution and, after three hours, the conversion into acid was shown to be complete by titration with standard aqueous barium hydroxide. The solution was acidified, the liberated acid thoroughly extracted with ether and, after desiccation, polarimetrically examined in acetone solution:

$$l = 2,\ c = 1{\cdot}0880,\ a_D + 3{\cdot}45°,\ [a]_D + 158{\cdot}6°.$$

The pure *d*-acid has $[a]_D^{15{\cdot}5}$ + 173·4° when dissolved in acetone.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the cost of the investigation.

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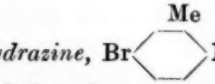
XLVII.—*Derivatives of Bromotolylhydrazines.*

By Frederick Daniel Chattaway and George Dufour Hodgson.

The bromotolylhydrazines have been studied by Michaelis (*Ber.*, 1893, **26**, 2192), who obtained *p*-bromo-*o*-tolylhydrazine by brominating acetyl-*o*-tolylhydrazine, and by Hewitt and Pope (T., 1898, **73**, 174), who prepared *o*-bromo-*p*-tolylhydrazine from *o*-bromo-*p*-toluidine and described a number of its derivatives. In the course of an investigation of substituted hydrazides and hydrazones, undertaken on account of the frequent occurrence of polymorphic modifications among them, a number of other derivatives of these hydrazines have been prepared.

The bromotolylhydrazines are both easily prepared from the corresponding bromotoluidines, the acetyl derivatives of which are readily obtained by the direct bromination of aceto-*o*- and *p*-toluidides. They are solid, well-crystallised substances which form stable salts, but, like other hydrazines, are readily oxidised when exposed to the air. When oxidised either by oxygen or by alkaline oxidising agents they both yield *m*-bromotoluene, the action taking the usual course (Chattaway, T., 1907, **91**, 1323; 1908, **93**, 270). They are converted into diazonium salts by halogens (Chattaway, T., 1908, **93**, 852; 1909, **95**, 1065), and undergo autoreduction when strongly heated (Chattaway and Aldridge, T., 1911, **99**, 404).

Experimental.

5-Bromo-o-tolylhydrazine,  .—The 5-bromoaceto-*o*-toluidide required for the preparation is most advantageously prepared by brominating aceto-*o*-toluidide in glacial acetic acid suspension. The product, after hydrolysis with alcoholic hydrochloric acid, was diazotised and reduced in the usual manner, and gave 5-bromo-*o*-tolylhydrazine identical with the compound obtained by Michaelis by the bromination of acetyl-*o*-tolylhydrazine.

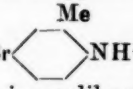
When strongly heated it decomposes into 5-bromo-*o*-toluidine, *m*-bromotoluene, nitrogen, and ammonia. It is readily oxidised by Fehling's solution or alkaline chromate, yielding *m*-bromotoluene and nitrogen.

3-Bromoaceto-*p*-toluidide (m. p. 117·5°) was prepared in an exactly similar manner from aceto-*p*-toluidide, and similarly converted into 3-bromo-*p*-toluidine (m. p. 22°), which furnished

3-bromo-*p*-tolylhydrazine (Found, Br = 39·78. Calc., Br = 39·75 per cent.) melting at 94·2° (Michaelis gives 94·5—95°, and Hewitt and Pope 91°). On exposure to air it rapidly oxidises, turning brown and yielding *m*-bromotoluene and nitrogen.

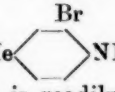
Acetyl-3-bromo-*p*-tolylhydrazine (Found, Br = 33·14. Calc., Br = 32·88 per cent.) crystallises from alcohol in colourless, short prisms with pyramidal ends, which melt at 130·5° (Hewitt and Pope give 124°).

Both hydrazines yield benzoyl and nitrobenzoyl derivatives when they are brought into contact with the corresponding chlorides in the presence of dilute alkali hydroxides or pyridine.

Benzoyl-5-bromo-o-tolylhydrazine,  , crystallises from boiling alcohol, in which it is readily soluble, in colourless needles melting at 172·5°:

0·1893 gave 0·1166 AgBr. Br = 26·20.

$C_{14}H_{13}ON_2Br$ requires Br = 26·20 per cent.

Benzoyl-3-bromo-p-tolylhydrazine,  , crystallises from boiling alcohol, in which it is readily soluble, in long, slender, colourless hexagonal prisms melting at 144°:

0·1230 gave 0·0755 AgBr. Br. = 26·12.

$C_{14}H_{13}ON_2Br$ requires Br = 26·20 per cent.

The nitrobenzoyl derivatives are best prepared by dissolving equivalent amounts of the hydrazine and nitrobenzoyl chloride in ether and adding an equivalent amount of pyridine.

o-*Nitrobenzoyl-5-bromo-o-tolylhydrazine* crystallises from boiling glacial acetic acid, in which it is readily soluble, giving a bright yellow solution, in clusters of bright yellow, compact, flattened prisms melting at 179°:

0·2268 gave 0·1272 AgBr. Br = 22·86.

$C_{14}H_{12}O_3N_3Br$ requires Br = 22·82 per cent.

o-*Nitrobenzoyl-3-bromo-p-tolylhydrazine* is readily soluble in boiling alcohol or boiling glacial acetic acid, from which it crystallises in tufts of pale yellow, very slender prisms melting at 177°:

0·1548 gave 0·0826 AgBr. Br = 22·71.

$C_{14}H_{12}O_3N_3Br$ requires Br = 22·82 per cent.

m-*Nitrobenzoyl-3-bromo-o-tolylhydrazine* is readily soluble in boiling glacial acetic acid, giving a pale yellow solution, from which it crystallises in tufts of canary-yellow, very slender prisms melting and decomposing at 185°:

0·1288 gave 0·0671 AgBr. Br = 22·69.

$C_{14}H_{12}O_3N_3Br$ requires Br = 22·82 per cent.

m-*Nitrobenzoyl*-3-*bromo*-p-*tolylhydrazine* is readily soluble in boiling glacial acetic acid, giving a very pale yellow solution, from which it crystallises in tufts of bright orange-coloured, slender prisms melting at 171°:

0·1741 gave 0·0950 AgBr. Br = 22·69.

$C_{14}H_{12}O_3N_3Br$ requires Br = 22·82 per cent.

p-*Nitrobenzoyl*-5-*bromo*-o-*tolylhydrazine* is readily soluble in boiling alcohol or glacial acetic acid, from which it crystallises in clusters of bright yellow prisms melting and decomposing at 199°:

0·2482 gave 0·1055 AgBr. Br = 22·77.

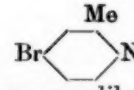
$C_{14}H_{12}O_3N_3Br$ requires Br = 22·82 per cent.

p-*Nitrobenzoyl*-3-*bromo*-p-*tolylhydrazine* crystallises from boiling alcohol or boiling glacial acetic acid, in both of which it is moderately readily soluble, in bright orange, short, flattened prisms with domed ends melting at 159·5°:

0·1975 gave 0·1053 AgBr. Br = 22·69.

$C_{14}H_{12}O_3N_3Br$ requires Br = 22·82 per cent.

Both hydrazines readily react with aldehydes, forming well-crystallised hydrazones which, unless otherwise stated, were prepared by mixing alcoholic solutions of equivalent amounts of hydrazine and aldehyde.

Benzaldehyde-5-*bromo*-o-*tolylhydrazone*, 

crystallises from alcohol, in which it is very readily soluble, in large, pale yellow rhombic plates melting at 107·5°:

0·1650 gave 0·1067 AgBr. Br = 27·53.

$C_{14}H_{13}N_2Br$ requires Br = 27·66 per cent.

On keeping, this compound quickly decomposed, forming a dark red, tarry mass. This is noteworthy, as the isomeric benzaldehyde-3-bromo-*p*-tolylhydrazone kept for the same length of time showed no change.

p-*Nitrobenzaldehyde*-5-*bromo*-o-*tolylhydrazone* crystallises from boiling glacial acetic acid, in which it is moderately readily soluble, in short, stout, ruby-red prisms melting and decomposing at 185°:

0·1257 gave 0·0703 AgBr. Br = 23·82.

$C_{14}H_{12}O_2N_3Br$ requires Br = 23·93 per cent.

o-*Nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone* is very sparingly soluble in boiling alcohol and readily so in boiling glacial acetic acid, from which it crystallises in compact, four-sided, brilliant scarlet rhombic plates melting at 178°:

0·2126 gave 0·1200 AgBr. Br = 24·03.

$C_{14}H_{12}O_2N_3Br$ requires Br = 23·93 per cent.

m-*Nitrobenzaldehyde*-5-*bromo*-o-*tolylhydrazone* crystallises from boiling glacial acetic acid, in which it is sparingly soluble, in tufts of slender, needle-shaped orange crystals melting at 216·5°:

0·1220 gave 0·0688 AgBr. Br = 24·01.

$C_{14}H_{12}O_2N_3Br$ requires Br = 23·93 per cent.

m-*Nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone* is very sparingly soluble in boiling alcohol or glacial acetic acid, from which it crystallises in short, stout, flattened orange prisms melting at 174°:

0·1843 gave 0·1036 AgBr. Br = 23·92.

$C_{14}H_{12}O_2N_3Br$ requires Br = 23·93 per cent.

p-*Nitrobenzaldehyde*-5-*bromo*-o-*tolylhydrazone* crystallises from boiling glacial acetic acid, in which it is moderately readily soluble, in long, slender, ruby-red prisms melting at 213°:

0·2306 gave 0·1282 AgBr. Br = 23·67.

$C_{14}H_{12}O_2N_3Br$ requires Br = 23·93 per cent.

p-*Nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone* is sparingly soluble in boiling alcohol and moderately readily so in boiling glacial acetic acid, from which it crystallises in long, stout, brilliant red prisms melting at 154·5°:

0·1300 gave 0·0729 AgBr. Br = 23·84.

$C_{14}H_{12}O_2N_3Br$ requires Br = 23·93 per cent.

Salicylaldehyde-5-*bromo*-o-*tolylhydrazone* crystallises from alcohol, in which it is very readily soluble, in colourless, hexagonal prisms with pyramidal ends melting at 105·5°:

0·1986 gave 0·1226 AgBr. Br = 26·27.

$C_{14}H_{13}ON_2Br$ requires Br = 26·18 per cent.

Anisaldehyde-5-*bromo*-o-*tolylhydrazone* is very readily soluble in alcohol, from which it crystallises in colourless, elongated, flattened prisms melting at 95·5°.

On keeping, it soon decomposes to a dark red, tarry mass. This is noteworthy, as the 3-bromo-*p*-tolyl compound shows no change on keeping for the same length of time:

0·1835 gave 0·1078 AgBr. Br = 25·05.

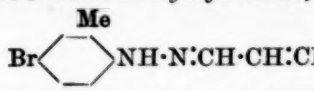
$C_{15}H_{15}ON_2Br$ requires Br = 25·12 per cent.

Anisaldehyde-3-*bromo*-p-*tolylhydrazone* crystallises from boiling alcohol, in which it is readily soluble, in long, colourless needles melting at 89°:

0·1391 gave 0·0819 AgBr. Br = 25·06.

$C_{15}H_{15}ON_2Br$ requires Br = 25·12 per cent.

Cinnamaldehyde-3-bromo-o-tolylhydrazone,



is readily soluble in boiling alcohol or boiling glacial acetic acid, giving orange-coloured solutions, from which it crystallises in large, orange-coloured plates melting at 160°:

0·1930 gave 0·1160 AgBr. Br = 25·58.

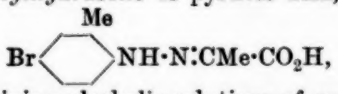
$C_{16}H_{15}N_2Br$ requires Br = 25·39 per cent.

*Cinnamaldehyde-3-bromo-*p*-tolylhydrazone* is readily soluble in boiling alcohol or boiling glacial acetic acid, giving bright yellow solutions, from which it crystallises in tufts of thin, slender, bright canary-yellow plates melting at 120°:

0·1744 gave 0·1038 AgBr. Br = 25·33.

$C_{16}H_{15}N_2Br$ requires Br = 25·39 per cent.

The *5-bromo-o-tolylhydrazone* of pyruvic acid,

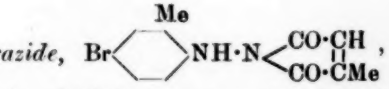


was prepared by mixing alcoholic solutions of equivalent quantities of pyruvic acid and 3-bromo-*o*-tolylhydrazine. Vigorous action took place, and the mass set to a solid mass of crystals. It is readily soluble in alcohol or glacial acetic acid, from both of which it crystallises in pale yellow, stout, short hexagonal prisms melting and decomposing at 180·5°:

0·2452 gave 0·1711 AgBr. Br = 29·42.

$C_{10}H_{11}O_2N_2Br$ requires Br = 29·48 per cent.

Both hydrazines readily react with citraconic and phthalic anhydrides when heated together on the water-bath in the presence of a little alcohol.

Citraconyl-5-bromo-o-tolylhydrazide, 

crystallises from boiling alcohol, in which it is very readily soluble, in deep yellow, short, stout prisms with pyramidal ends melting at 176°:

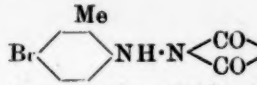
0·1228 gave 0·0784 AgBr. Br = 27·19.

$C_{12}H_{11}O_2N_2Br$ requires Br = 27·09 per cent.

*Citraconyl-3-bromo-*p*-tolylhydrazide* crystallises from alcohol, in which it is very readily soluble, in bright yellow prisms melting at 102°:

0·1022 gave 0·0652 AgBr. Br = 27·16.

$C_{12}H_{11}O_2N_2Br$ requires Br = 27·09 per cent.

Phthalyl-5-bromo-o-tolylhydrazide, 

crystallises from alcohol, in which it is sparingly soluble, in pale yellow, slender prisms melting at 194°. It is readily soluble in boiling glacial acetic acid:

0·1876 gave 0·1048 AgBr. Br = 24·02.

$C_{15}H_{11}O_2N_2Br$ requires Br = 24·16 per cent.

Phthalyl-3-bromo-p-tolylhydrazide is readily soluble in boiling glacial acetic acid, giving a bright yellow solution, from which it crystallises in bright yellow, very slender needles melting at 162°:

0·1245 gave 0·0705 AgBr. Br = 24·10.

$C_{15}H_{11}O_2N_2Br$ requires Br = 24·16 per cent.

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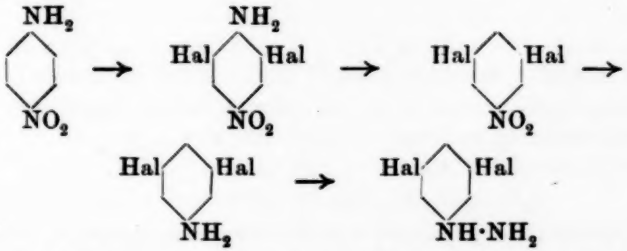
XLVIII.—3 : 5-*Dibromo- and* 3 : 5-*Dichloro-phenylhydrazine.*

By FREDERICK DANIEL CHATTAWAY and OSCAR CHARLES ELLINGTON.

THESE hydrazines were prepared by the usual methods from the corresponding anilines. The anilines, which are troublesome to prepare in quantity, were obtained by brominating or chlorinating *p*-nitroaniline, removing the amino-group from the 2 : 6-dihalogen-4-nitroaniline thus produced, and reducing the 3 : 5-dihalogen-nitrobenzene, thus:



The 3 : 5-dihalogen-substituted phenylhydrazines resemble phenylhydrazine closely in behaviour, are easily oxidised by air or oxidising agents, giving *m*-dibromo- or *m*-dichloro-benzene, react with halogen to produce diazonium salts, and yield with acid anhydrides and aldehydes stable and characteristic hydrazides and hydrazones.

Experimental.

3:5-*Dibromophenylhydrazine hydrochloride*, $C_6H_3Br_2 \cdot N_2H_3,HCl$, was prepared by dissolving 3:5-dibromoaniline in a small quantity of glacial acetic acid, adding concentrated hydrochloric acid in excess, and stirring vigorously until a thin paste of the hydrochloride was produced. This was then diazotised at 0° and added to the calculated quantity of stannous chloride dissolved in concentrated hydrochloric acid cooled to 0°. The 3:5-dibromophenylhydrazine hydrochloride, which separated as a cream-coloured paste, was filtered off and crystallised from boiling dilute hydrochloric acid, in which it is moderately readily soluble, separating in colourless, slender, flattened prisms.

On heating, it darkens in colour, and decomposes without previously melting at about 207°:

0·2079 gave 0·3534 AgBr + AgCl. Cl = 11·61; Br = 52·36.

$C_6H_7N_2ClBr_2$ requires Cl = 11·72; Br = 52·86 per cent.

3:5-*Dibromophenylhydrazine* was obtained from the hydrochloride by heating for a short time with excess of aqueous sodium hydroxide. The hydrazine, which solidified on cooling, was crystallised from alcohol, in which it is very readily soluble; it separated in colourless, small, elongated plates melting at 95·5°:

0·1976 gave 0·2768 AgBr. Br = 59·61.

$C_6H_6N_2Br_2$ requires Br = 60·14 per cent.

It is slowly oxidised by the air and rapidly oxidised when heated with Fehling's solution or a solution of potassium chromate, yielding nitrogen and *m*-dibromobenzene.

It can only be preserved unchanged if sealed up and protected from light; if kept in a stoppered bottle exposed to light and air, it soon shows signs of decomposition.

3:5-*Dichlorophenylhydrazine hydrochloride*, which was prepared exactly as the dibromo-compound, is moderately readily soluble in boiling dilute hydrochloric acid, from which it crystallises in colourless, small, irregular plates. On heating, these decompose without previously melting at about 190°:

0·1602 gave 0·3207 AgCl. Cl = 49·53.

$C_6H_7N_2Cl_3$ requires Cl = 49·84 per cent.

3:5-*Dichlorophenylhydrazine* crystallises from alcohol, in which it is very readily soluble, in colourless, small, elongated plates melting at 118°:

0·1912 gave 0·3056 AgCl. Cl = 39·56.

$C_6H_6N_2Cl_2$ requires Cl = 40·06 per cent.

It quickly oxidises and turns brown in the air, producing nitro-

gen and *m*-dichlorobenzene. The same action takes place quantitatively when it is oxidised by Fehling's solution or hot aqueous potassium chromate. The 3 : 5-dihalogen-substituted hydrazines readily form hydrazides when acetylated, benzolated, or heated with phthalic or citraconic anhydride.

Acetyl-3 : 5-dibromophenylhydrazine, $C_6H_3Br_2 \cdot NH \cdot NH \cdot CO \cdot CH_3$, is very readily soluble in alcohol, from which it crystallises in slender, colourless prisms melting at 198·5° :

0·1920 gave 0·2341 AgBr. Br = 51·89.

$C_8H_8ON_2Br_2$ requires Br = 51·90 per cent.

Acetyl-3 : 5-dichlorophenylhydrazine crystallises from alcohol, in which it is readily soluble, in colourless, slender, flattened prisms melting at 175·5° :

0·2259 gave 0·2948 AgCl. Cl = 32·29.

$C_8H_8ON_2Cl_2$ requires Cl = 32·38 per cent.

Benzoyl-3 : 5-dibromophenylhydrazine,

$C_6H_3Br_2 \cdot NH \cdot NH \cdot CO \cdot C_6H_5$,

crystallises from alcohol, in which it is readily soluble, in slender, colourless plates melting at 206° :

0·1478 gave 0·1492 AgBr. Br = 42·95.

$C_{13}H_{10}ON_2Br_2$ requires Br = 43·20 per cent.

Benzoyl-3 : 5-dichlorophenylhydrazine crystallises from alcohol, in which it is readily soluble, in clusters of small, colourless plates melting at 221·5° :

0·1918 gave 0·1946 AgCl. Cl = 25·11.

$C_{13}H_{10}ON_2Cl_2$ requires Cl = 25·22 per cent.

o-*Nitrobenzoyl-3 : 5-dibromophenylhydrazine* crystallises from boiling alcohol or glacial acetic acid, in both of which it is moderately readily soluble, giving pale yellow solutions, in clusters of small, elongated, very pale yellow plates melting at 204° :

0·2036 gave 0·1840 AgBr. Br = 38·45.

$C_{13}H_9O_3N_3Br_2$ requires Br = 38·51 per cent.

o-*Nitrobenzoyl-3 : 5-dichlorophenylhydrazine* is moderately readily soluble in boiling alcohol, giving a bright yellow solution, from which it crystallises in slender, very pale yellow, elongated prisms melting at 218·5° :

0·2118 gave 0·1855 AgCl. Cl = 21·68.

$C_{13}H_9O_3N_3Cl_2$ requires Cl = 21·75 per cent.

m-*Nitrobenzoyl-3 : 5-dibromophenylhydrazine* is sparingly soluble in boiling alcohol, giving a pale yellow-coloured solution, from which it crystallises in very faintly yellow-coloured, slender prisms melting at 235° :

0·1688 gave 0·1534 AgBr. Br = 38·66.

$C_{13}H_9O_3N_3Br_2$ requires Br = 38·51 per cent.

m-*Nitrobenzoyl*-3:5-*dichlorophenylhydrazine* crystallises from alcohol, in which it is sparingly soluble, in long, slender, pale yellow prisms melting at 235·5°:

0·2872 gave 0·2508 AgCl. Cl = 21·60.

$C_{13}H_9O_3N_3Cl_2$ requires Cl = 21·75 per cent.

p-*Nitrobenzoyl*-3:5-*dibromophenylhydrazine* is sparingly soluble in alcohol and moderately readily so in boiling glacial acetic acid, from which it crystallises in tufts of bright yellow, very slender prisms melting at 200°:

0·1150 gave 0·1039 AgBr. Br = 38·44.

$C_{13}H_9O_3N_3Br_2$ requires Br = 38·51 per cent.

p-*Nitrobenzoyl*-3:5-*dichlorophenylhydrazine* is sparingly soluble in alcohol and readily so in boiling glacial acetic acid, from which it crystallises in pale yellow, very slender, hair-like prisms melting at 196°:

0·2082 gave 0·1828 AgCl. Cl = 21·72.

$C_{13}H_9O_3N_3Cl_2$ requires Cl = 21·75 per cent.

Citraconyl-3:5-*dibromophenylhydrazide*,

$$C_6H_3Br_2\cdot NH\cdot N\begin{matrix}CO\cdot CH\\ \|\\ CO\cdot CMe\end{matrix},$$

is readily soluble in benzene, from which it crystallises in compact, bright yellow prisms melting at 155°:

0·2595 gave 0·2706 AgBr. Br = 44·36.

$C_{11}H_8O_2N_2Br_2$ requires Br = 44·39 per cent.

Citraconyl-3:5-*dichlorophenylhydrazide* crystallises from alcohol or benzene, in both of which it is very readily soluble, in bright yellow, compact prisms with domed ends melting at 156·5°:

0·2202 gave 0·2310 AgCl. Cl = 25·95.

$C_{11}H_8O_2N_2Cl_2$ requires Cl = 26·16 per cent.

The 3:5-dihalogen-substituted phenylhydrazines yield with aldehydes and ketones stable, well-crystallised hydrazones. They are, as a rule, easily prepared by mixing an alcoholic solution of the hydrazine with an alcoholic solution of the equivalent amount of the corresponding aldehyde or ketone and adding a little glacial acetic acid, which appears much to facilitate the reaction.

Benzaldehyde-3:5-*dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N{:}CHPh,$$

crystallises from alcohol, in which it is readily soluble giving a very pale yellow solution, in stout, rhombic, very faint yellow plates melting at 117·5°:

0·2130 gave 0·2294 AgCl. Cl = 26·64.

$C_{13}H_{10}N_2Cl_2$ requires Cl = 26·75 per cent.

When exposed to light it quickly becomes bright scarlet, which may be due to rearrangement of the molecule to an azo-configuration:

$$C_6H_3Cl_2\cdot NH\cdot N{:}CHPh \longrightarrow C_6H_3Cl_2\cdot N{:}N\cdot CH_2Ph,$$

a rearrangement which has been suggested as an explanation of the striking change of colour which the unsubstituted hydrazone undergoes when similarly exposed to light.

o-*Nitrobenzaldehyde*-3 : 5-*dibromophenylhydrazone* is moderately readily soluble in boiling glacial acetic acid, from which it crystallises in long, bright scarlet, needle-shaped, flattened prisms melting and decomposing at 224°:

0·2111 gave 0·1983 AgBr. Br = 39·98.

$C_{13}H_9O_2N_3Br_2$ requires Br = 40·05 per cent.

o-*Nitrobenzaldehyde*-3 : 5-*dichlorophenylhydrazone* crystallises from alcohol, in which it is moderately readily soluble, in bright scarlet, very small, slender prisms melting at 222°:

0·2568 gave 0·2316 AgCl. Cl = 22·32.

$C_{13}H_9O_2N_3Cl_2$ requires Cl = 22·87 per cent.

m-*Nitrobenzaldehyde*-3 : 5-*dibromophenylhydrazone* is very sparingly soluble in boiling glacial acetic acid, giving a bright yellow solution, from which it crystallises in clusters of bright, orange-coloured, very small, flattened prisms melting at 233°:

0·2437 gave 0·2292 AgBr. Br = 40·03.

$C_{13}H_9O_2N_3Br_2$ requires Br = 40·05 per cent.

m-*Nitrobenzaldehyde*-3 : 5-*dichlorophenylhydrazone* is very sparingly soluble in boiling glacial acetic acid, giving a bright yellow solution, from which it crystallises in clusters of minute, flattened, bright orange prisms melting at 205°:

0·4124 gave 0·3780 AgCl. Cl = 22·69.

$C_{13}H_9O_2N_3Cl_2$ requires Cl = 22·87 per cent.

p-*Nitrobenzaldehyde*-3 : 5-*dibromophenylhydrazone* exists in two polymorphous modifications. It is sparingly soluble in boiling glacial acetic acid, giving a bright orange coloured solution, from which it crystallises, on rapidly cooling, in long, slender, orange-coloured prisms; small, irregular, six-sided red plates, melting at 242°, soon make their appearance in the liquid and grow at the expense of the orange-coloured modification, which dissolves and finally disappears.

0·2436 gave 0·2293 AgBr. Br = 40·05.

$C_{13}H_9O_2N_3Br_2$ requires Br = 40·05 per cent.

p-*Nitrobenzaldehyde*-3 : 5-*dichlorophenylhydrazone* also exists in

two polymorphous modifications. It is sparingly soluble in boiling glacial acetic acid, giving a bright orange-coloured solution, from which it crystallises in long, slender, orange-coloured prisms, which similarly transform into clusters of minute, scarlet, six-sided plates melting at 238·5°:

0·1884 gave 0·1735 AgCl. Cl = 22·79.

$C_{13}H_9O_2N_3Cl_2$ requires Cl = 22·87 per cent.

Salicylaldehyde-3:5-*dibromophenylhydrazone* is very readily soluble in alcohol, from which it crystallises in pale yellow plates melting at 141·5°:

0·2111 gave 0·2137 AgBr. Br = 43·07.

$C_{13}H_{10}ON_2Br_2$ requires Br = 43·30 per cent.

Salicylaldehyde-3:5-*dichlorophenylhydrazone* crystallises from alcohol, in which it is very readily soluble, in glistening, very faint yellow plates melting at 146°:

0·2309 gave 0·2350 AgCl. Cl = 25·19.

$C_{13}H_{10}ON_2Cl_2$ requires Cl = 25·23 per cent.

Anisaldehyde-3:5-*dibromophenylhydrazone* is very readily soluble in boiling alcohol, from which it crystallises in colourless prisms melting at 130°:

0·2296 gave 0·2243 AgBr. Br = 41·58.

$C_{14}H_{12}ON_2Br_2$ requires Br = 41·62 per cent.

Anisaldehyde-3:5-*dichlorophenylhydrazone* crystallises from boiling alcohol, in which it is readily soluble, in clusters of very slender, colourless prisms melting at 127°:

0·2250 gave 0·2179 AgCl. Cl = 23·97.

$C_{14}H_{12}ON_2Cl_2$ requires Cl = 24·03 per cent.

Cinnamaldehyde-3:5-*dibromophenylhydrazone*,

$$C_6H_3Br_2\cdot NH\cdot N{:}CH\cdot CH{:}CHPh,$$

is fairly readily soluble in boiling alcohol, giving a bright yellow solution, from which it crystallises in glistening, yellow plates melting at 150°:

0·1654 gave 0·1624 AgBr. Br = 41·79.

$C_{15}H_{12}N_2Br_2$ requires Br = 42·06 per cent.

Cinnamaldehyde-3:5-*dichlorophenylhydrazone* crystallises from boiling alcohol, in which it is very readily soluble, giving a bright yellow solution, in pale yellow, long, flattened prisms melting at 142°:

0·2348 gave 0·2302 AgCl. Cd = 24·25.

$C_{15}H_{12}N_2Cl_2$ requires Cl = 24·36 per cent.

The 3:5-*dibromophenylhydrazone* of pyruvic acid,

$$C_6H_3Br_2\cdot NH\cdot N{:}CMe\cdot CO_2H,$$

is very readily soluble in alcohol, from which it crystallises in very pale yellow, almost colourless, prisms melting and decomposing at 192°:

0·2454 gave 0·2739 AgBr. Br = 47·49.

$C_9H_8O_2N_2Br_2$ requires Br = 47·57 per cent.

The 3:5-*dichlorophenylhydrazone* of pyruvic acid crystallises from alcohol, in which it is very readily soluble, in very pale yellow, slender prisms melting at 192°:

0·1970 gave 0·2276 AgCl. Cl = 28·59.

$C_9H_8O_2N_2Cl_2$ requires Cl = 28·70 per cent.

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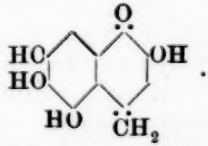
XLIX.—2-*Hydroxy*-1-*keto*-4-*methylene*-1 : 4-*dihydronaphthalene*.

By HARRY FITZGIBBON DEAN and MAXIMILIAN NIERENSTEIN.

THE present investigation was undertaken with the view of preparing the ground for the continuation of our work on purpurogallin (Nierenstein and Spiers; *Ber.*, 1913; **46**, 3151; Dean and Nierenstein; *ibid.*, 3868) to which compound we have temporarily assigned the formula of 2:5:6:7-tetrahydroxy-1-keto-4-methylene-1:4-dihydronaphthalene:



2-*Hydroxy*-1-*keto*-4-*methylene*-1:4-*dihydronaphthalene* (II) is obtained by the action of pyridine on 2-hydroxy-1-keto-4-dicarbethoxymethylene-1:4-dihydronaphthalene (I), which is prepared according to Sachs and Craveri's method (*Ber.*, 1905, **38**, 3694), both the saponification of the ethyl groups and the elimination of the carboxyl groups taking place simultaneously:

(I.) (II.)

The proportions used by us in the preparation of the compound are: 25 c.c. of pyridine to 5 grams of the ester. The solution, which at once turns dark blue, is heated for 8—10 hours, and the greater part of the pyridine then removed by distillation. On acidification a dark-red product is obtained, which crystallises from glacial acetic acid in deep red needles melting and decomposing at about 248—250°. Similar needles are also obtained on crystallisation from *s*-tetrachloroethane. On addition of alkali to the aqueous or alcoholic solution of 2-hydroxy-1-keto-4-methylene-1:4-dihydronaphthalene a blue colour is produced, which turns red on acidification. These very sensitive colour reactions have been measured for us by Dr. G. S. Walpole in his work on indicators (*Biochem. J.*, 1914, **8**, 632):

0·2035 gave 0·5735 CO_2 and 0·0894 H_2O. C = 76·86; H = 4·92.
$C_{11}H_8O_2$ requires C = 76·75; H = 4·65 per cent.

When oxidised with dilute nitric acid (compare Dean and Nierenstein, *loc. cit.*) *dihydroxyhemimellitic acid* was obtained, which gave the same melting point as found for this acid prepared by us from purpurogallin. (Found, *C = 44·85; H = 3·31. $C_9H_6O_8$ requires C = 44·63; H = 2·48 per cent.)

The distillation of the substance with zinc dust gave naphthalene, which had the correct melting point when crystallised from alcohol. The formation of naphthalene confirms the views expressed by Hooker (T., 1896, **69**, 1355), and also by us (*loc. cit.*) as to the possible elimination of the side-chain during the distillation with zinc dust, since both Hooker's lapachol and our purpurogallin formulæ require the formation of 4-methylnaphthalene and not naphthalene.

The *acetyl* derivative, $C_{11}H_7O_2{\cdot}CO{\cdot}CH_3$, is prepared in the usual way by heating 2-hydroxy-1-keto-4-methylene-1:4-dihydronaphthalene with acetic anhydride. It crystallises from ethyl acetate in long, lemon-yellow needles which melt and decompose at 212—213°:

0·1335 gave 0·3562 CO_2 and 0·0568 H_2O. C = 72·77; H = 4·77.
$C_{13}H_{10}O_3$ requires C = 72·89; H = 4·68 per cent.

The acetyl derivative yields a *phenylhydrazone*,

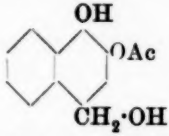
$$C_{13}H_{10}O_2H{:}N{\cdot}NHPh,$$

on dissolving in glacial acetic acid and warming on the water-bath with a slight excess of phenylhydrazine. It crystallises from glacial acetic acid in dark red needles melting and decomposing at about 278—281°:

0·1090 gave 8·7 c.c. N_2 (moist) at 17° and 766 mm. N = 9·33.
$C_{19}H_{17}O_2N_3$ requires N = 9·22 per cent.

* Dried at 50° in a vacuum.

If 2-hydroxy-1-keto-4-methylene-1 : 4-dihydronaphthalene is treated with acetic anhydride and a trace of concentrated sulphuric acid and then poured into absolute alcohol, the product is the acetyl derivative described above. The same compound is also obtained when calcium carbonate is added to neutralise the sulphuric acid and the filtrate concentrated under diminished pressure. On the other hand, if the solution is poured into water there is obtained *1-hydroxy-2-acetoxynaphthyl-4-carbinol*:



The same compound is also produced if 2-acetoxy-1-keto-4-methylene-1 : 4-dihydronaphthalene is dissolved in glacial acetic acid, dilute sulphuric acid added, and the solution diluted with water. It crystallises from alcohol in colourless needles melting at 189—190°:

0·1348* gave 0·3364 CO_2 and 0·0558 H_2O. C = 68·06; H = 4·64.
0·1737 † „ 0·4282 CO_2 „ 0·0794 H_2O. C = 67·23; H = 5·12.
$C_{13}H_{12}O_4$ requires C = 67·24; H = 5·18 per cent.

The *methoxy*-derivative, $C_{11}H_7O_2Me$, is prepared by the action of diazomethane in ethereal suspension. It crystallises from alcohol in long, yellow needles melting at 184—185°:

0·1542 gave 0·4383 CO_2 and 0·0742 H_2O. C = 77·53; H = 5·39.
$C_{12}H_{10}O_2$ requires C = 77·42; H = 5·39 per cent.

The *phenylhydrazone*, $C_{12}H_{10}O{:}N{\cdot}NHPh$, crystallises from glacial acetic acid in deep red plates melting and decomposing at about 254—257°:

0·1004 gave 8·9 c.c. N_2 (moist) at 18° and 760 mm. N = 10·28.
$C_{18}H_{16}ON_2$ requires N = 10·15 per cent.

If 2-methoxy-1-keto-4-methylene-1 : 4-dihydronaphthalene is dissolved in acetic acid, dilute sulphuric acid added, and then water, it is converted into the corresponding *1-hydroxy-2-methoxynaphthyl-4-carbinol*, $OH{\cdot}C_{10}H_5(OMe){\cdot}CH_2{\cdot}OH$, which crystallises from alcohol in colourless needles melting at 172–173°:

0·1159 gave 0·3012 CO_2 and 0·0624 H_2O. C = 70·87; H = 6·03.
$C_{12}H_{12}O_3$ requires C = 70·58; H = 5·89 per cent.

The carbinol yields on methylation with diazomethane 1 : 2-*dimethoxynaphthyl-4-carbinol*, $C_{10}H_5(OMe)_2{\cdot}CH_2{\cdot}OH$, which crystallises from benzene in colourless needles melting at 148—150°. Apparently also here, as in the case of some other carbinols (compare

* Dried at 170 –175°. † Dried at 120—125°.

Geake and Nierenstein, T., 1915, **107**, 1491) the hydroxyl group of the carbinol radicle is not methylated by diazomethane:

0·1290 gave 0·3375 CO_2 and 0·0884 H_2O. C = 71·36; H = 7·66.
$C_{13}H_{14}O_3$ requires C = 71·56; H = 6·43 per cent.

An ethereal solution containing molecular proportions of 2-methoxy-1-keto-4-methylene-1:4-dihydronaphthalene and 1-hydroxy-2-methoxynaphthyl-4-carbinol yields the corresponding *quinhydrone*, which crystallises from ether in brown prisms melting and decomposing at 219°:

0·2175 gave 0·5864 CO_2 and 0·1120 H_2O. C = 73·53; H = 5·77.
$C_{24}H_{22}O_5$ requires 73·84; H = 5·65 per cent.

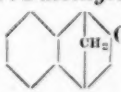
2-*Methoxy*-1:4-*ethylcarbonatomethylenenaphthalene*,

(R = CH·C·CO_2Et).

This product is formed on shaking molecular proportions of 2-methoxy-1-keto-4-methylene-1:4-dihydronaphthalene, ethyl chlorocarbonate and sodium hydroxide. The resulting solid is obtained after several crystallisations from alcohol in colourless, silky needles melting at 126—127°. If warmed with dilute pyridine or dilute acetic acid the original 2-methoxy-1-keto-4-methylene-1:4-dihydronaphthalene and not 1-hydroxy-2-methoxynaphthyl-4-carbinol is recovered, which conclusively proves its constitution. In addition to the usual analysis, a hydroxyl estimation according to Daniel and Nierenstein's method (*Ber.*, 1911, **44**, 701) was also made:

0·1680* gave 0·4297 CO_2 and 0·0823 H_2O. C = 69·75; H = 5·49.
0·2846 „ 0·0493 CO_2. CO_2 = 17·32 (Daniel and Nierenstein).
$C_{15}H_{14}O_4$ requires C = 69;76; H = 5·43; CO_2 = 17·06 per cent.

2-*Methoxy*-1:4-*methylenenaphthalene*,



This substance is formed when 2-methoxy-1-keto-4-methylene-1:4-dihydronaphthalene is reduced with an excess of sodium amalgam. It crystallises from dilute acetic acid in fine, colourless, glistening needles which melt and decompose at 208°:

0·1939 gave 0·5998 CO_2 and 0·0968 H_2O. C = 84·47; H = 5·59.
$C_{12}H_{10}O$ requires C = 84·71; H = 5·89 per cent.

The *benzylidene* derivative, $C_{12}H_8O{:}CHPh$, is readily prepared

* The combustion was carried out in oxygen (see Francis and Nierenstein *Annalen*, 1911, **382**, 202).

by heating the substance described above with benzaldehyde in the presence of acetic anhydride and anhydrous sodium acetate. It crystallises from dilute alcohol in rosettes of prisms, melting and decomposing at 224—226°:

0·1722 gave 0·5568 CO_2 and 0·0922 H_2O. C = 88·18; H = 5·99.
$C_{19}H_{14}O$ requires C = 88·36; H = 5·42 per cent.

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L.—*The Action of Water on Cupric Thiocyanate.*

By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

SOME time ago (T., 1913, **103**, 795) the authors published the results of a research on the progressive change which solutions of ferric thiocyanate undergo. Even at the ordinary temperature and in an indifferent atmosphere, the ferric iron is reduced, whilst a corresponding oxidation of the thiocyanogen radicle takes place. The investigation of this reaction brought out the novel and interesting fact that the great bulk of the carbon which is thus oxidised is eliminated in the form of carbon dioxide.

It appeared probable that the change which cupric thiocyanate undergoes in contact with water might be of the same character, and that carbon dioxide might be produced in this case also. A simple experiment designed to test this point gave a positive result, and it was therefore decided to examine in some detail the action of water on cupric thiocyanate.

It has been long known that the black precipitate obtained on mixing solutions of cupric salts with alkali thiocyanates is slowly acted on by water, the copper being finally converted into cuprous thiocyanate. The reaction attracted the attention of several investigators about eighty years ago, and attempts were made to identify the products of change other than the cuprous salt. Claus (*J. pr. Chem.*, 1838, **15**, 401) and Meitzendorff particularly (*Ann. Phys. Chem.*, 1842, [ii], **56**, 88) showed that amongst these other products were thiocyanic, hydrocyanic, and sulphuric acids, but the efforts of the latter author to find a satisfactory quantitative basis for the reaction were unsuccessful. So far as can be discovered, there is no record in the literature of any investigation carrying the problem beyond the point at which it was left by Meitzendorff.

Experimental.

The vessel in which the reaction took place was a large bottle or round-bottomed flask, provided with a trebly-bored rubber stopper. Through two of the holes there passed glass tubes, one of which reached almost to the bottom of the vessel, and admitted a current of air or nitrogen, freed from carbon dioxide, the other providing for the passage of the escaping gases to the train of absorption flasks. The third hole carried the stem of a dropping funnel, from which a measured quantity of the cupric salt (chloride or acetate) could be delivered into the excess of alkali thiocyanate solution previously placed in the flask. The precipitate formed in the reaction vessel was kept in intimate contact with water by shaking the vessel until the completion of the change—a period of ten to twenty days, according to the conditions.

With the object of making a quantitative study of the reaction, and on the basis of the experience gained in the examination of ferric thiocyanate solutions, preparations were first made to estimate hydrogen cyanide, carbon dioxide, sulphuric acid, and ammonia. The first two of these substances were drawn out of the reaction mixture by means of an aspirator and absorbed in successive trains of flasks containing silver nitrate and baryta solutions respectively. The reaction vessel, containing the alkali thiocyanate solution, and the absorption flasks, containing the silver nitrate and the baryta, were filled from the beginning with air or nitrogen freed from carbon dioxide.

The preliminary experiments showed that it was desirable to have more than one flask containing silver nitrate solution, for, although the absorption of hydrogen cyanide was complete in the first flask, there was formed, even in a second flask, a very small quantity of a black precipitate, arising apparently from the hydrolysis of some compound by the silver nitrate. Experience showed that a train of four silver nitrate flasks was adequate, the formation of the black precipitate never being observed in any flask beyond the third. When too few silver nitrate flasks were employed, sulphide was found in the first succeeding flask containing baryta solution. It is suggested that the black precipitate is silver sulphide, arising from the hydrolysis of a trace of carbonyl sulphide produced in the reaction. The quantity of this black precipitate was extremely small and it was not estimated.

The carbon dioxide was estimated by absorption in a train of flasks charged with known quantities of standard baryta solution, the excess of baryta being found by subsequent titration with standard oxalic acid solution. A complication arose when the cupric salt employed for the production of the cupric thiocyanate

was the acetate, for in this case cyanogen is formed and passes off through the silver nitrate solution into the baryta solution. Here it is hydrolysed, giving rise to cyanide, carbon dioxide, and ammonia, and its amount was ascertained by estimating the cyanide in the baryta flasks, subsequent to the titration with oxalic acid. The result obtained in this way was checked by a determination of the ammonia in the united contents of the baryta flasks. From the cyanide found, the quantity of carbon dioxide produced by the hydrolysis of the cyanogen was calculated, and deducted from the total quantity of carbon dioxide absorbed in the baryta.

The sulphuric acid and the ammonia arising from the action of water on cupric thiocyanate would naturally remain in the reaction mixture, which becomes increasingly acid as the change proceeds. In order, therefore, to estimate these two substances, aliquot portions of the filtrate from the cuprous thiocyanate finally obtained were employed. The estimation of the sulphuric acid presented no difficulty. One characteristic, however, of the ammonia determination, observed in the earlier experiments, indicated that, in addition to thiocyanic acid and ammonium salts, the reaction mixture contained some other nitrogenous compound, for the expulsion of the ammonia never came to a definite end, but continued for hours. There was evidently present some nitrogenous compound slowly hydrolysed by boiling alkali hydroxide, and carbamide was accordingly suspected. The presence of this compound was definitely established by the xanthhydrol test (Fosse, *Compt. rend.*, 1913, **157**, 948), and it was finally estimated by the soja-bean method, after the ammonia had been removed by treatment with alkali hydroxide at 40—50° and aspiration (compare Plimmer and Skelton, *Biochem. J.*, 1914, **8**, 70). The hydrobromite method of estimating the carbamide, after the removal of the ammonia, was also employed, but was not found so satisfactory.*

So far, then, as the merely qualitative side of the investigation is concerned, it is clear that the action of water on cupric thiocyanate, formed by mixing cupric chloride with excess of potassium thiocyanate, leads to the production of the following substances, in addition to cuprous thiocyanate: Carbon dioxide, hydrogen cyanide, ammonia, sulphuric acid, and carbamide. Further, as found by Meitzendorff, considerable quantities of thiocyanic acid are formed during the reaction. When, on the other hand, the cupric thiocyanate is obtained by mixing cupric acetate with excess

* The presence of carbamide in ferric thiocyanate solutions which have been allowed to remain for some time was also proved with the aid of the soja-bean method. This observation probably accounts for the previously unexplained deficiency of nitrogen in the recognised products of the action of water on ferric thiocyanate (T., 1913, **103**, 796).

of potassium thiocyanate, the products of the action of water include cyanogen as well as the substances just specified.

That the foregoing list covers all the products of the action of water on cupric thiocyanate, with the possible exception of any, such as carbonyl sulphide, which occur in mere traces, appears certain from a consideration of the quantitative results of the investigation. It is clear that if no essential product has escaped detection, then, in any particular experiment, the total quantities of carbon, nitrogen, and sulphur found in one or other of the substances estimated should be in the atomic ratio 1:1:1, since they arise from the oxidation of the thiocyanogen radicle. It is further plain that, in applying this test, the quantities of cuprous thiocyanate and thiocyanic acid need not be considered, since these compounds contain the thiocyanogen radicle intact.

The data for the four final experiments only are recorded below, no account being taken of the many preliminary and incomplete trials which were made before carbamide was definitely detected and estimated in the reaction products.

Experiment I.

2000 *c.c. potassium thiocyanate solution containing* 100 *grams* KCNS.

250 *c.c. cupric chloride solution containing* 9·25 *grams* Cu.

	Found.	C.	N.	S.
CO_2	0·412	0·1124	—	—
NH_3	0·1376	—	0·1133	—
HCN.....	0·242	0·1076	0·1255	—
H_2SO_4	1·860	—	—	0·6073
$CO(NH_2)_2$	0·0795	0·0159	0·0371	—
		0·2359	0·2759	0·6073
Atomic ratio		1	1	0·96

Experiment II.

100 *c.c. potassium thiocyanate solution containing* 20 *grams* KCNS.

125 *c.c. cupric chloride solution containing* 4·12 *grams* Cu.

775 *c.c. water.*

	Found.	C.	N.	S.
CO_2	0·221	0·0603	—	—
NH_3	0·0680	—	0·0560	—
HCN	0·0798	0·0355	0·0414	—
H_2SO_4	0·900	—	—	0·294
$CO(NH_2)_2$	0·0619	0·0124	0·0289	—
		0·1082	0·1263	0·294
Atomic ratio		1	1	1·02

Experiment III.

1500 *c.c. potassium thiocyanate solution containing* 80 *grams* KCNS.

500 *c.c. cupric acetate solution containing* 10·2 *grams* Cu.

	Found.	C.	N.	S.
CO_2	0·646	0·1762	—	—
NH_3	0·239	—	0·1968	—
HCN	0·0498	0·0221	0·0258	—
H_2SO_4	2·228	—	—	0·7275
C_2N_2	0·1144	0·0528	0·0616	—
$CO(NH_2)_2$	0·0334	0·0067	0·0156	—
		0·2578	0·2998	0·7275
Atomic ratio		1	0·997	1·06

Experiment IV.

100 *c.c. potassium thiocyanate solution containing* 20 *grams* KCNS.

200 *c.c. cupric acetate solution containing* 4·08 *grams* Cu.

700 *c.c. water.*

	Found.	C.	N.	S.
CO_2	0·273	0·0745	—	—
NH_3	0·097	—	0·0800	—
HCN.....	0·0207	0·0092	0·0107	—
H_2SO_4	0·947	—	—	0·3092
C_2N_2	0·059	0·0272	0·0317	—
$CO(NH_2)_2$.....	0·0319	0·0064	0·0149	—
		0·1173	0·1373	0·3092
Atomic ratio		1	1·004	0·988

The figures recorded in the foregoing tables show that the action of water on cupric thiocyanate is restricted to the production of the substances specified, but, in order to account for the appearance even of those, it is necessary to assume the occurrence of fairly complicated reactions. Without attempting to indicate the mechanism of these reactions, one may suggest the following equations as representing the different ways in which water acts on cupric thiocyanate, equations based on the assumption that in each reaction the products account for an equal number of carbon, nitrogen, and sulphur atoms:

(*a*) $8Cu(CNS)_2 + 6H_2O = 8CuCNS + 7HCNS + CO_2 + \underbrace{NH_3 + H_2SO_4}$

(*b*) $6Cu(CNS)_2 + 4H_2O = 6CuCNS + 5HCNS + HCN + H_2SO_4$

(*c*) $14Cu(CNS)_2 + 8H_2O = 14CuCNS + 12HCNS + C_2N_2 + 2H_2SO_4$

(*d*) $16Cu(CNS)_2 + 11H_2O = 16CuCNS + 14HCNS + CO_2 + CO(NH_2)_2 + 2H_2SO_4$.

It is possible to test the appropriateness of these equations by comparing the final acidity of the reaction mixture, which was determined in each of the four experiments detailed above, with the acidity calculated on the basis of the equations. In experiment I, for example, the filtrate from the cuprous thiocyanate was made up to three litres, and the solution was then found to be 0·0508*N* in regard to acid. On the other hand, the number of equivalents of acid which should be formed according to equation (*a*), the calculation being based on the quantity of ammonia found, is $\frac{0{\cdot}1376 \times 8}{17} = 0{\cdot}0648$. Similarly, the number of equivalents of acid formed according to equation (*b*) and the amount of hydrogen cyanide found should be $\frac{0{\cdot}242 \times 7}{27} = 0{\cdot}0627$. Finally, the number of equivalents of acid formed according to equation (*d*) and the quantity of carbamide found should be $\frac{0{\cdot}0795 \times 18}{60} = 0{\cdot}0238$. In all, the number of equivalents of acid which, on the basis of the equations proposed, should be formed in experiment I, is 0·1513. If the solution containing this quantity of acid were made up to 3 litres, as was actually done, it would then be 0·0504*N* in regard to acid, a figure which agrees closely with the experimental value quoted above.

The extent of the agreement between the observed and calculated figures for the final acidity in the other experiments is seen from the following table:

	Acidity calculated.	Acidity found.
Experiment II.	0·0713*N*	0·0709*N*
„ III.	0·0855*N*	0·0895*N*
„ IV.	0·0789*N*	0·0790*N*

It thus appears that the equations proposed are in fact capable of representing satisfactorily the relation between the experimentally determined quantities of the various reaction products.

Summary.

(1) When cupric chloride solution is mixed with excess of potassium thiocyanate solution, the precipitated cupric thiocyanate is slowly acted on by the water present. Reduction to cuprous thiocyanate is ultimately complete, and the other products formed concurrently are carbon dioxide, ammonia, carbamide, hydrogen cyanide, thiocyanic and sulphuric acids.

(2) When the cupric thiocyanate is obtained by acting on cupric

acetate with excess of potassium thiocyanate, a further product of the reaction, in addition to those already specified, is cyanogen.

(3) A quantitative basis for the action of water on cupric thiocyanate is supplied by the equations proposed on page 601.

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LI.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part II.*

By PRAFULLA CHANDRA RÂY.

THE investigation described in the previous paper (this vol., p. 131) has been continued, with the result that many new and interesting facts have been brought to light. The product of the interaction of mercury methylmercaptide nitrite and butyl iodide was expected to conform with the formula Me_2S_2,HgI_2,C_4H_9I, but repeated analyses of different preparations gave values for the percentage of iodine which were invariably too low. The compound was purified by repeated crystallisation and melted sharply at 108°, and, moreover, the analyses agreed fairly well among themselves. It was therefore subjected to a thorough and systematic examination. The carbon-content was also estimated with the precautions necessary in the case of sulphur compounds. The remarkable fact was elicited that, during the course of the above interaction, an intermolecular change occurs and the light radicle methyl is displaced by the heavy butyl.

The first stage of the reaction seems to be as follows:

$$Me_2S_2 + HgI\,* + C_4H_9{\cdot}NO_2,$$

but owing to the tendency to form the disulphonium compound, the reaction readily enters on the second stage thus:

$$\begin{matrix} Me_2S_2 & HgI \\ \nwarrow & \\ & C_4H_9I \end{matrix}, \; C_4H_9I \quad \text{or} \quad MeS_2{\cdot}C_4H_9,HgI_2,C_4H_9I,$$

or it is equally probable that, in the initial stages before the MeS· groups unite together, and exchange of the methyl and butyl radicles takes place, resulting in the formation of the product in question.

* The intermediate formation of mercurous iodide is supported by the fact that on shaking the mercury mercaptide nitrite even in the cold with an alkyl iodide containing free iodine the colour of the liquid is at once discharged.

As has been pointed out in the previous communication, a nitroparaffin and its isomeride, a nitrite, are also formed in the reaction; intermolecular change on exactly similar lines takes place when ethyl, propyl, and amyl iodides are substituted for butyl iodide. In other words, in the course of the formation of the present series of disulphonium compounds, the light radicle methyl is invariably displaced by its higher homologues. It is remarkable that in substituted ammonium compounds the reverse is the case; the radicle methyl displacing heavy radicles like benzyl, ethyl, allyl, etc. (T., 1907, **91**, 2083). Indirectly, we have here a method of obtaining the mixed disulphides of the type $R{\cdot}S_2{\cdot}R'$, although as yet no suitable means has been found of isolating these from the above compounds. As will be shown below, however, since these disulphonium salts can be synthesised by the direct combination of an alkyl disulphide with mercuric iodide and an alkyl iodide, we can fairly presume the existence of mixed disulphides in the present series.

With the view of ascertaining if a similar displacement takes place in the case of ethyl, mercury ethylmercaptide nitrite was treated with an excess of propyl, butyl, and amyl iodides respectively. It was found that when the compound was treated with *n*-propyl iodide, no such displacement of radicles took place in the first experiment, but on repeating the preparation, the expected displacement occurred. It is not easy to explain this behaviour, except on the supposition that it is a case of mass action; for, on heating mercury ethylmercaptide nitrite with an excess of methyl iodide under reflux, the heavier radicle ethyl is also found to be displaced by methyl, giving rise to the compound $MeEtS_2,HgI_2,MeI$. This evidently offers the best solution of the anomaly. It is very likely that in the first experiment, a large excess of propyl iodide was not used. On treatment with butyl and amyl iodides, the compounds obtained also had the formulæ $EtS_2{\cdot}C_4H_9,HgI_2,C_4H_9I$ and $EtS_2{\cdot}C_5H_{11},HgI_2,C_5H_{11}I$ respectively.

It has been found, however, that when once the compound Me_2S_2,HgI_2,MeI has been formed, the methyl radicle can no longer be displaced by a higher homologue; for instance, on digesting this salt with butyl iodide, the composition remained unchanged; evidently it is only in the nascent state that this displacement takes place.

Another striking feature is the position of the three iodine atoms in the chain. Accepting the typical formula for the series as:

$$\begin{array}{c} R\ HgI \\ |\ \ | \\ R\text{-}S\text{-}S\text{-}R' \\ |\ \ | \\ I\ I \end{array}.$$

where R and R′ represent alkyl radicles, the iodine atoms linked directly to the sulphur atoms might be expected to occupy a position different from that in the complex group HgI. In acetone solution, at any rate, no such distinction is perceptible, as all the three atoms of iodine are removed as silver iodide on treatment with an acetone solution of silver nitrate. The reaction has been found to be quantitative, and on it has been based the estimation of iodine in these compounds. As described in the previous paper, the iodine had to be estimated by heating the compounds with powdered copper and boiling the cuprous iodide thus formed with alkali hydroxide. This method is tedious and laborious, and the iodine is usually found too low by 1 or 2 per cent., whereas the present method is as exact, rapid, and expeditious as the estimation of halogens in soluble haloids by means of a standard solution of silver nitrate. Conversely, by treating a disulphonium alkyl mercuri-iodide with silver nitrate, or any other silver salt soluble in acetone, in molecular proportions, the corresponding nitrate, etc., can be easily prepared as shown below. For the estimation of mercury, however, heating with copper powder would appear to give the best results. The salts no doubt can be dissolved in *aqua regia* or in concentrated nitric acid (Carius's method), but during the evaporation of the excess of acid some of the mercury is lost by volatilisation, owing to the formation of chloride or iodide of mercury. Carius's method of dissolution liberates free iodine, which again is taken up by the mercury in solution during evaporation, forming the iodide. It has generally been found that the result is too low by 1 to 1·5 per cent. by the latter method.

Mercury Mercaptide Nitrites and the Corresponding Disulphonium Compounds of Heavy Complex Radicles.

The wide field which the interaction covers and its range of comprehensive applicability are further evidenced by the fact that mercury mercaptide nitrites of complex radicles also give rise to the expected disulphonium compounds. Thus, 2-mercaptothiazoline, $\begin{matrix}CH_2-S\\ |\\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot SH$ and ethylene mercaptan, $C_2H_4(SH)_2$, yield the corresponding mercury mercaptide nitrites, $\begin{matrix}CH_2-S\\ |\\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot S\cdot HgNO_2$ and $C_2H_4(SHgNO_2)_2$, and these again by the action of an alkyl iodide, for example, ethyl iodide, are converted into:

$$\left[\begin{matrix}CH_2-S\\ |\\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot S\right]_2, HgI_2, EtI \quad \text{and} \quad (C_2H_4S_2)_2, HgI_2, EtI$$

respectively. The latter compound contains 4 atoms of sulphur,

of which only two are quadrivalent, and should be formulated according to the scheme proposed above in the following manner:

$$C_2H_4\begin{matrix}S\text{———}S\\ SEtI\cdot SI(HgI)\end{matrix}C_2H_4.$$

Experimental.

Interaction of Mercury Methylmercaptide Nitrite and Methyl Iodide: Formation of the Compound Me_2S_2,HgI_2,MeI.

The method of preparation in this, as also in the following series, was exactly the same as that described in the first communication, and need not be repeated. It may also be added here, once for all, that all the members of the series consist of bright yellow crystals. When these are purified by a second crystallisation, they resemble flowers of sulphur, having a pale yellow tint.

The salt as obtained above melted sharply at 162°. The first member of the series shows an anomalous behaviour in this respect; the succeeding ones, even with the introduction of heavier radicles, have much lower melting points.

0·1619 gave 0·0326 CO_2 and 0·0256 H_2O. C = 5·49; H = 1·76.
0·3963 „ 0·1141 Hg. Hg = 28·79.
0·0630 required 11·4 c.c. $AgNO_3$ (acetone solution) * = 2·74 c.c. $N/10$-$AgNO_3$. I = 55·24.
$C_3H_9I_3S_2Hg$ requires C = 5·22; H = 1·30; Hg = 28·98; I = 55·21 per cent.

Interaction of Mercury Methylmercaptide Nitrite and Ethyl Iodide: Formation of the Compound $MeEtS_2,HgI_2,EtI$.

The salt melted sharply at 67°:

0·2278 gave 0·0676 CO_2 and 0·0416 H_2O. C = 8·09; H = 2·03.
0·3594 „ 0·1004 Hg. Hg = 27·93.
0·2744 required 47·6 c.c. $AgNO_3$ (acetone solution) = 11·46 c.c. $N/10$-$AgNO_3$. I = 53·01.
$C_5H_{13}I_3S_2Hg$ requires C = 8·36; H = 1·82; Hg = 27·86; I = 53·06 per cent.

Interaction of Mercury Methylmercaptide Nitrite and n-*Propyl Iodide.*

The product has the formula $MePr^nS_2,HgI,Pr^nI$ (compare this vol., p. 137):

* The acetone solution was necessarily very dilute; it was standardised against $N/10$-sodium chloride.

0·1554 gave 0·0610 CO_2 and 0·0341 H_2O. C=10·70; H=2·50.
The compound previously described gave Hg=27·15, 27·52; I=51·15.
$C_7H_{17}I_3S_2Hg$ requires C=11·26; H=2·28; Hg=26·81; I=51·07 per cent.

Interaction of Mercury Methylmercaptide Nitrite and n-*Butyl Iodide: Formation of the Compound* $MeS_2 \cdot C_4H_9, HgI_2, C_4H_9I$.

The crystals melted sharply at 108°:

0·2048 gave 0·1034 CO_2 and 0·0516 H_2O. C=13·77; H=2·80.
0·2440 „ 0·0636 Hg and 0·2193 AgI. Hg=26·07; I=48·56.
$C_9H_{21}I_3S_2Hg$ requires C=13·95; H=2·71; Hg=25·84; I=49·22 per cent.

Interaction of Mercury Methylmercaptide Nitrite and iso*Amyl Iodide: Formation of the Compound* $MeS_2 \cdot C_5H_{11}, HgI_2, C_5H_{11}I$.

On adding ether to the acetone solution of the crude product, a brownish, light oil separated out, which turned into a semi-solid, yellowish-green mass:

0·1541 gave 0·0908 CO_2 and 0·0485 H_2O. C=16·07; H=3·50.
0·2826 „ 0·0730 Hg. Hg=25·82.
0·1214 required 18·9 c.c. $AgNO_3$ (acetone solution)=4·55 c.c. $N/10$-$AgNO_3$=0·0578 I. I=47·61.
$C_{11}H_{25}I_3S_2Hg$ requires C=16·46; H=3·12; Hg=24·93; I=47·50 per cent.

Interaction of 2-Mercaptothiazoline and Ethyl Iodide: Formation of the Compound $\begin{matrix} CH_2\text{–}S \\ | \\ CH_2\cdot N \end{matrix}\!\!>\!C\cdot S.HgNO_2$.

2-Mercaptothiazoline in alcoholic solution was treated with mercuric nitrite solution, when a white, crystalline precipitate was obtained, which, on being dried in a vacuum desiccator, turned pale yellow. The substance gave the characteristic tests of a nitrite:

0·0890 gave 0·0296 CO_2 and 0·0160 H_2O. C=9·04; H=2·00.
0·0844 „ 5·2 c.c. N_2 at 25° and 760 mm. N=7·25.
0·1328 „ 0·1686 $BaSO_4$ and 0·0820 HgS. S=17·44; Hg=53·22.
$C_3H_4O_2NS_2Hg$ requires C=9·89; H=1·10; N=7·69; S=17·58; Hg=54·94 per cent.

The above salt was treated with ethyl iodide in the usual way, and the expected disulphonium compound,

$$\left(\begin{matrix}CH_2\text{–}S\\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot S\right)_2,HgI_2,EtI,$$

was formed as a yellowish-brown solid.

0·1523 gave 0·0613 CO_2 and 0·0338 H_2O. C = 19·98; H = 2·47.
0·1319 „ 2·7 c.c. N_2 at 24° and 760 mm. N = 2·41.
0·2275 „ 0·0540 Hg. Hg = 23·74.
0·0482 required 7·85 c.c. $AgNO_3$ (acetone solution) = 1·7 c.c. $N/10$-$AgNO_3$ = 0·0216 I. I = 44·80.

$C_8H_{13}N_2I_3S_4Hg$ requires C = 11·35; H = 1·54; N = 3·31; Hg = 23·64; I = 45·03 per cent.

It is noteworthy that mercury 2-mercaptothiazoline nitrite, although it contains a tertiary nitrogen atom, has not the capacity of fixing a molecule of ethyl iodide, giving rise to a quaternary ammonium iodide. Evidently the proximity of 2 atoms of sulphur deprives it of this power.

Mercury Ethylenemercaptide Nitrites and their Reaction with Ethyl Iodide.

By the interaction of dithiolethylene and mercuric nitrite, two distinct mercury mercaptide nitrites of the formulæ $HgNO_2\cdot S\cdot C_2H_4\cdot S\cdot HgNO_2$ and $HgNO_2\cdot S\cdot C_2H_4\cdot S_2\cdot C_2H_4\cdot S\cdot HgNO_2$, are simultaneously formed, and it is not an easy matter to isolate them in a state of purity. The nitrous fumes evolved in the first stage of the reaction $[-SH + Hg(NO_2)_2 = -S\cdot HgNO_2 + HNO_2]$ act as an oxidising agent, giving rise to mercury diethylenemercaptide nitrite. The tendency towards the formation of polythioglycols has already been referred to by V. Meyer (*Ber.*, 1886, **19**, 3264). By using a dilute solution of ethylene mercaptan in alcohol, the liability to oxidation can, as far as one can make out, be minimised and a larger yield of the first compound secured. As will be shown below, it is immaterial for our purpose whether the one or the other, or a mixture of both, is treated with an alkyl iodide, for the disulphonium compound obtained will be the same, namely, $(C_2H_4S_2)_2,HgI_2,RI$. The analysis given below indicates the compound of the second formula with a slight admixture of that of the first:

0·1174 gave 0·0302 CO_2 and 0·0184 H_2O. C = 7·02; H = 1·74.
0·0747 „ 2·6 c.c. N_2 at 24° and 760 mm. N = 4·09.
0·0706 „ 0·0510 HgS. Hg = 62·27.

$C_4H_8O_4N_2S_4Hg_2$ requires C = 7·10; H = 1·18; N = 4·14; Hg = 59·17 per cent.

Another preparation, which evidently consisted mainly of a salt of the first formula, gave:

C=5·76; H=1·42; Hg=65·92.

$C_2H_4O_4N_2S_2Hg_2$ requires C=4·11; H=0·69; Hg=68·50 per cent.

These mercury mercaptide nitrites are crystalline and white, with a faint pink tint. They evolve nitrous fumes when treated with hydrochloric acid.

The above salts, when treated with ethyl iodide, yielded a disulphonium compound of the formula

$$C_2H_4\begin{matrix}S_2\\S_2\end{matrix}>C_2H_4,HgI_2,EtI.$$

0·1536 gave 0·0560 CO_2 and 0·034 H_2O. C=9·94; H=2·45.

0·3002 „ 0·0756 Hg. Hg=24·99.

0·0392 required 6·8 c.c. $AgNO_3$ (acetone solution)=1·47 c.c. $N/10$-$AgNO_3$=0·01867 I. I=47·62.

$C_6H_{13}I_3S_4Hg$ requires C=9·07; H=1·64; Hg=25·19; I=47·98 per cent.

Interaction of Mercury Ethylmercaptide Nitrite and n-*Propyl Iodide.*

The product of this interaction (Et_2S_2,HgI_2,Pr^nI) has been described in the previous paper. Estimation of carbon and hydrogen confirmed the formula already given:

0·1558 gave 0·0656 CO_2 and 0·0409 H_2O. C=11·48; H=2·92.

$C_7H_{17}I_3S_2Hg$ requires C=11·26; H=2·28 per cent.

On repeating the preparation, however, a crystalline product, $EtPr^nS_2,HgI_2,Pr^nI$ (m. p. 77°), of a deeper orange-yellow colour was obtained, in which it was found that the ethyl radicle has been exchanged for propyl:

0·1827 gave 0·0842 CO_2 and 0·0474 H_2O. C=12·57; H=2·88.

0·0744 required 14·2 c.c. $AgNO_3$ (acetone solution)=2·93 c.c. $N/10$-$AgNO_3$=0·0372 I. I=50·07.

$C_8H_{19}I_3S_2Hg$ requires C=12·63; H=2·5; I=50·13 per cent.

Interaction of Mercury Ethylmercaptide Nitrite and n-*Butyl Iodide: Formation of the Compound* $EtS_2{\cdot}C_4H_9,HgI_2,C_4H_9I$.

The product obtained in this case was not crystalline, but a dark liquid of treacle-like consistency. This is the first instance in which an anomaly in the higher members of the series is encountered. In this case there is an exchange of the lighter radicle ethyl for the heavier radicle butyl:

0·1721 gave 0·0956 CO_2 and 0·0578 H_2O. C = 15·15; H = 3·73.*
0·0268 required 4·75 c.c. $AgNO_3$ (acetone solution) = 1·02 c.c. $N/10$-$AgNO_3$ = 0·01295 I. I = 48·33.
$C_{10}H_{23}I_3S_2Hg$ requires C = 15·23; H = 2·92; I = 48·35 per cent.

Interaction of Mercury Ethylmercaptide Nitrite and iso*Amyl Iodide: Formation of the Compound* $EtS_2 \cdot C_5H_{11},HgI_2,C_5H_{11}I$.

The product obtained was treacle-like as before. Here also the displacement of radicles takes place:

0·1955 gave 0·1308 CO_2 and 0·0612 H_2O. C = 18·24; H = 3·48.
0·2796 „ 0·0695 Hg. Hg = 24·86.
0·0522 required 9·3 c.c. $AgNO_3$ (acetone solution) = 1·92 c.c. $N/10$-$AgNO_3$ = 0·02438 I. I = 46·71.
$C_{12}H_{27}I_3S_2Hg$ requires C = 17·65; H = 3·31; Hg = 24·51; I = 46·69 per cent.

Interaction of Mercury Ethylmercaptide Nitrite and Methyl Iodide.

The pale yellow, crystalline product melted at 84—85°, and corresponded with the formula $MeEtS_2,HgI_2,MeI$ (compare this vol., p. 136):

0·1662 gave 0·0398 CO_2 and 0·0286 H_2O. C = 6·53; H = 1·91.
0·0738 required 18·9 c.c. $AgNO_3$ (acetone solution) = 3·15 c.c. $N/10$-$AgNO_3$ = 0·0400 I. I = 54·19.
$C_4H_{11}I_3S_2Hg$ requires C = 6·82; H = 1·56; I = 54·11 per cent.

The Nitrates of the Series: Formation of the Compound $MePr^nS_2,Hg(NO_3)_2,Pr^nNO_3,C_3H_6O$.

This compound was obtained, as explained before, by double decomposition between the corresponding iodide and silver nitrate in acetone solution. It is a viscid liquid, which contains a molecular proportion of acetone:

0·1400 gave 0·1088 CO_2 and 0·0552 H_2O. C = 21·19; H = 4·38.
0·0767 „ 4·6 c.c. N_2 at 23° and 760 mm. N = 7·09.
0·2254 „ 0·8620 HgS. Hg = 32·96.
$C_7H_{17}O_9N_3S_2Hg,C_3H_6O$ requires C = 19·71; H = 3·78; N = 6·90; Hg = 32·84 per cent.

* Minute traces of vapour of mercuric iodide are sometimes carried into the calcium chloride tube, thus slightly increasing the percentage of hydrogen in this and in some other estimations.

Formation of the Compound $Et_2S_2,Hg(NO_3)_2,Pr^nNO_3,C_3H_6O$.

This compound * resembles the former, and also combines with a molecular proportion of acetone:

0·1190 gave 0·0900 CO_2 and 0·0534 H_2O. C = 20·62; H = 4·98.
0·0833 „ 5·4 c.c. N_2 at 23° and 760 mm. N = 7·67.
0·1346 „ 0·0500 HgS. Hg = 32·02.

$C_7H_{17}O_9N_3S_2Hg$ requires C = 19·71; H = 3·78; N = 6·90; Hg = 32·84 per cent.

It will be noticed that both the compounds have the same molecular weight and the same number of carbon atoms.

Formation of the Compound Et_2S_2,HgI_2,EtI.

Ethyl disulphide and mercuric iodide in molecular proportions are heated under reflux with an excess of ethyl iodide on a water-bath for three hours. On cooling, a yellow, crystalline mass is obtained. The dark mother liquor, consisting chiefly of ethyl iodide, on evaporation leaves a small quantity of a viscid residue. The crystalline product is dissolved in acetone and precipitated by addition of ether, and further purified by recrystallisation. The fine yellow crystals thus obtained melt at 110° and conform to the formula Et_2S_2,HgI_2,EtI, and are indistinguishable from the product obtained by the interaction of mercury ethylmercaptide nitrite and ethyl iodide as already described. It should be noted here that Hilditch and Smiles, by treating the above components in acetone solution, obtained a salt of the formula Et_2S,HgI_2,EtI, that is, a disulphonium derivative (T., 1907, **91**, 1397). It is not clear why a disulphide should yield a derivative of the alkyl monosulphide.

0·1588 gave 0·0540 CO_2 and 0·0353 H_2O. C = 9·27; H = 2·47.
0·7253 „ 0·4657 $BaSO_4$.† S = 8·82.
0·2888 „ 0·0779 Hg. Hg = 26·97.
0·0824 required 14 c.c. $AgNO_3$ (acetone solution) = 3·37 $N/10$-$AgNO_3$ = 0·0428 I. I = 51·94.

$C_6H_{15}I_3S_2Hg$ requires C = 9·84; H = 2·05; S = 8·74; Hg = 27·32; I = 52·05 per cent.

* This preparation was made from the sample in which no interchange of radicle took place. See p. 288.

† The method of analysis has been explained in the previous communication (this vol., p. 135). The substance, heated with copper powder, gives up both its iodine and sulphur to the latter, forming cuprous iodide and sulphide respectively. The cuprous iodide is converted into sodium iodide by treatment with sodium hydroxide solution. The residue, now consisting of cuprous sulphide, is fused with pure sodium nitrate and carbonate and then lixiviated with hot water. The sulphur is thus obtained in the filtrate as sodium sulphate and estimated in the usual way.

Hilditch and Smiles's salt melted at 110° and requires S=4·57 per cent. It would thus appear that they really obtained a derivative, not of the monosulphide, but of the disulphide.

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LII.—*Hydrates of Aluminium Nitrate.*

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NUMEROUS references to hydrates of aluminium nitrate are contained in the literature. In the majority of cases only the hydrate with 18 molecules of water, $Al_2(NO_3)_6,18H_2O$, is described, but, in addition, statements are made that the nitrate crystallises with 15, with 16, with 9, and with 4 molecules of water. In most cases, each worker appears to assume that no other form exists than that which he himself describes, but Jovitschitsch (*Monatsh.*, 1912, **33**, 16) describes a hydrate to which he assigns the formula $Al_2(NO_3)_6,15H_2O$, and recognises as differing from that with 18 molecules. Incidentally, it may be remarked that Jovitschitsch ascribes very remarkable properties to the crystals he obtained.

During the course of a protracted technical research on the action of nitric acid on aluminium, it has been observed that the nitrate may crystallise in at least three forms which differ appreciably from one another in habit, conditions of stability, solubility in concentrated nitric acid, and vapour pressure. To these three forms the following formulæ have been assigned:

$Al_2(NO_3)_6,18H_2O$;
$Al_2(NO_3)_6,15H_2O$ or $16H_2O$;
$Al_2(NO_3)_6,12H_2O$.

When aluminium is left in contact with a limited quantity of nitric acid (D 1·42) at 20°, very slow dissolution of the metal takes place, but the acid rapidly becomes saturated with aluminium nitrate, and large, clear, colourless crystals are deposited which grow in size and number until the bulk of the aluminium has been dissolved. While a sample of aluminium was being removed from a bottle containing a mass of these crystals, attention was first drawn to the fact that the nitrate crystallises in more than one form.

During the operation the solution, which had been quite clear, was seen to become clouded by a mass of small needles, which

rapidly formed a layer several mm. thick upon the original crystals at the bottom of the bottle. Simultaneously, the latter lost their transparency and changed into a white, opaque mass.

It appeared certain that the changes observed were due to the fact that the original deposit was composed of crystals of aluminium nitrate, which were unstable in the existing conditions, and that they had been transformed into a more stable and less soluble form. It was assumed that the final form was the hydrate generally described as containing $18H_2O$ (compare Eakle, *Zeitsch. Kryst. Min.*, 1896, **26**, 585), and this assumption was confirmed by analysis. Some difficulty was experienced in preparing the crystals for analysis owing to the fact that, on the one hand, they deliquesce very easily, and, on the other, readily part with water of crystallisation to drying agents. By pressing between filter papers, which had been recently dried, a sample was obtained which, on ignition, gave $Al_2O_3=13{\cdot}58$. The N_2O_5 content was estimated by the barium carbonate method and found to be 42·23. Theoretically, $Al_2(NO_3)_6,18H_2O$ should give $Al_2O_3=13{\cdot}62$ and $N_2O_5=43{\cdot}18$ per cent.

In subsequent experiments with nitric acid (D 1·42), it was generally found that at 20° unstable crystals were at first produced and that these ultimately changed into the stable hydrate containing $18H_2O$. An exception was observed in one case in which aluminium was dissolved in nitric acid in the presence of carbamide (0·3 gram of carbamide to 150 c.c. of acid). In that case the hydrate containing $18H_2O$ was deposited directly.

Under the microscope, the transformation from the unstable hydrate to the hydrate containing $18H_2O$ may be followed and seen to take place in three distinct stages. If a preparation of the unstable hydrate is inoculated with a crystal of the hydrate containing $18H_2O$, the latter is seen to throw out needles which soon impinge on the nearest crystals of the unstable hydrate. These immediately become opaque. Shortly after, they in turn throw out needles which, reaching other unchanged crystals, rapidly convert the whole mass into the hydrate containing $18H_2O$.

The composition of the stable hydrate having been determined, attempts were made to isolate and analyse the unstable form.

Saturated solutions of aluminium nitrate, prepared by heating the metal with nitric acid (D 1·42) and filtering through glass-wool, readily deposit abundant crops of these crystals on cooling. When such solutions are quickly cooled, the nitrate separates in the form of well-defined lozenges. By slow cooling, single crystals weighing several grams have often been obtained.

Three preparations, on ignition, gave $Al_2O_3=15{\cdot}5$, 15·56, and

15·5, figures which agree closely with the amount theoretically required for the hydrate $Al_2(NO_3)_6,13H_2O$, which demands Al_2O_3= 15·4 per cent. In spite of this close agreement, the results were not considered satisfactory, because it was noticed that before the crystals were completely freed from mother liquor they became opaque and suddenly dry. From this it was concluded that they had become transformed in so far as water was available in the mother liquor and that consequently the amount of water indicated by the analysis was too high.

An experiment was therefore made to obtain some indication of the existence of a hydrate with approximately $13H_2O$ by drying the stable hydrate containing $18H_2O$ over solid sodium hydroxide in a desiccator. This experiment pointed quite definitely to the existence of a hydrate having the composition $Al_2(NO_3)_6,12H_2O$, a result which all subsequent experiments confirmed. The progress of the dehydration of the hydrate containing $18H_2O$ was established by daily weighings, the following losses being noted:

Weight of salt taken = 2·5440 grams.

During the first	10	days	the daily loss averaged	0·110 gram.
„ next	10	„	„	0·0076 „
„ „	7	„	„	0·0090 „
„ „	10	„	„	0·0073 „
„ „	1	„	„	0·0006 „
„ „	3	„	„	0·0004 „

From these figures it was clear that after thirty-seven days a definite compound had been reached the rate of loss having fallen to little more than 1/20th of its previous value. The crystals were analysed, a correction being made for the loss of water during the last four days. They gave Al_2O_3=15·97, whereas the hydrate $Al_2(NO_3)_6,12H_2O$ requires Al_2O_3=15·95 per cent.

The crystals so far described were all produced by the action of nitric acid having D 1·42 on aluminium. The technical research, in the course of which these observations were made, required similar experiments with acid having D 1·5 at 20°. In this case crystals were also deposited, but there was no tendency to transformation, the crystals formed being quite stable in the more concentrated acid. The difficulties of preparing material for analysis were therefore much smaller, and numerous samples dried for varying periods on porous plate in a vacuum over solid sodium hydroxide gave concordant results agreeing with the formula $Al_2(NO_3)_6,12H_2O$.

It remains to be proved that the unstable hydrate produced in acid having D 1·42 is identical with the hydrate containing $12H_2O$, which is stable in acid having D 1·5.

The following proofs may be adduced:

(1) If aluminium is dissolved in hot concentrated acid (D 1·42) solutions are obtained which show to a marked extent the properties of supersaturation. From these solutions crystals of either the hydrate containing 12 or $18H_2O$ can be obtained by inoculation with crystals of these hydrates. It was found that the product, so far as could be determined, was identical, whether the solution was inoculated with a crystal of the hydrate containing $12H_2O$ derived from the solution of aluminium in acid having D 1·5, or by an unstable crystal derived from the solution in acid having D 1·42.

(2) Whilst the hydrate containing $12H_2O$ formed in acid having D 1·5 was quite stable in that acid, it proved unstable in acid having D 1·42, and underwent transformation into the hydrate containing $18H_2O$.

(3) On the other hand, the crystals first produced in acid having D 1·42 were found to be quite stable in acid having D 1·5, and this afforded a simple means of freeing them from the mother liquor, in which they were unstable. When washed with nitric acid having D 1·5 and dried on porous plate over solid sodium hydroxide in a vacuum, the crystals remained clear and to all appearances unchanged. After twenty-six days' exposure, they gave on ignition $Al_2O_3 = 15·75$. They were then finely powdered, when fumes of nitric acid, due to the occlusion of small quantities of mother liquor, were seen to be evolved. After two further days' exposure, they were again analysed and found to give $Al_2O_3 = 15·97$, whereas $Al_2(NO_3)_6,12H_2O$ requires $Al_2O_3 = 15·95$ per cent.

Some indication of the solubilities of the hydrates containing 12 and $18H_2O$ in nitric acid was obtained by noting the amount of aluminium dissolved when crystallisation commenced. In order to prevent supersaturation, the solutions were inoculated from time to time with crystal fragments of the hydrate the solubility of which was to be estimated. In acid having D 1·42 maintained at 20° the hydrate containing $18H_2O$ began to crystallise out when 0·109 gram of aluminium, equivalent to 1·52 grams of the hydrate $Al_2(NO_3)_6,18H_2O$, had dissolved in 100 grams of nitric acid.

When a crystal fragment of the hydrate containing $12H_2O$ was used as inoculant, crystallisation commenced, when 0·633 gram of aluminium, equivalent to 7·5 grams of the hydrate

$$Al_2(NO_3)_6,12H_2O,$$

had dissolved in 100 grams of nitric acid. The solubility of the hydrate containing $12H_2O$ is therefore much greater than that of the hydrate containing $18H_2O$.

The latter compound is not stable in acid having D 1·5, being

rapidly converted thereby into the former, but the approximate solubility of the hydrate containing $12H_2O$ in acid of the higher concentration was estimated in the same way. Crystallisation was found to begin when 0·0177 gram of aluminium, equivalent to 0·21 gram of the hydrate $Al_2(NO_3)_6,12H_2O$, had dissolved in 100 grams of nitric acid.

The Hydrate $Al_2(NO_3)_6,15$ or $16H_2O$.

The formation of this hydrate was first observed when examining a solution of nitrate prepared by dissolving aluminium in hot nitric acid (D 1·42), which had deposited a very fine crop of crystals of the hydrate $Al_2(NO_3)_6,12H_2O$. A few minutes after removing some of these crystals for analysis, the solution was found to contain a number of extremely thin plates, some of which had an area nearly 1 sq. cm. in extent. It was also seen that the crystals of the hydrate containing $12H_2O$ lost their sharp outline and became rugged in appearance. That the transformation observed was not the usual conversion of the hydrate containing $12H_2O$ into that containing $18H_2O$ was proved by the fact that after it was complete the solution was still supersaturated with regard to the latter, and gave a rich crop of crystals of the hydrate containing $18H_2O$ on being inoculated with a crystal of this material.

It was found that by using one of the new crystals as inoculant in an experiment made on a microscope slide, the transformation from the hydrate containing $12H_2O$ to that containing $18H_2O$ could be conducted in two stages. In the first, the hydrate containing 15 or $16H_2O$ was formed. On addition of a crystal of the hydrate containing $18H_2O$, the newly-formed crystals of the hydrate containing 15 or $16H_2O$ in turn underwent change, being converted into the former. By increasing the concentration of the nitric acid a solution was obtained in which the crystals of the hydrate containing 15 or $16H_2O$ were quite stable, but attempts to separate them from the mother liquor, as in the case of the other hydrates, frequently failed, owing to their transformation to the lower or higher hydrate before they were dry. The vapour pressures of the hydrates containing 18 and 15 or $16H_2O$ seem to lie very close together. Moreover, the slightest change in the amount of free nitric acid present entirely alters the conditions of stability of all the hydrates.

For the purpose of analysis a preparation of the new hydrate was allowed to remain for two days over solid sodium hydroxide in a desiccator. The crystals, which under the microscope appeared quite dry and unchanged, gave, on ignition, $Al_2O_3=14·5$.

$Al_2(NO_3)_6,15H_2O$ requires $Al_2O_3=14{\cdot}67$, whilst $Al_2(NO_3)_6,16H_2O$ requires $Al_2O_3=14{\cdot}3$ per cent.; so that in view of the difficulty of drying the crystals satisfactorily it is not at present possible to say by which formula they are represented.

Conclusions.

It has been shown that aluminium nitrate may crystallise in at least three forms, and the compositions of two of these have been determined as $Al_2(NO_3)_6,18H_2O$ and $Al_2(NO_3)_6,12H_2O$. The third hydrate probably crystallises with 15 or 16 molecules of water. The hydrate containing $12H_2O$ does not appear to have been described hitherto.

The hydrate containing $18H_2O$ is the most stable form at 20° in nitric acid having D 1·42 and is the least soluble.

In acid having D 1·5 at 20° the hydrate containing $12H_2O$ is alone stable.

The hydrate containing 15 or $16H_2O$ is stable in an acid of intermediate strength.

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LIII.—*Dyes Derived from Phenanthraquinone.*

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ON account of the close relationship between phenanthraquinone and anthraquinone, it may naturally be expected that suitable derivatives of phenanthraquinone will have valuable dyeing properties. This expectation is increased by the recorded properties of morpholquinone (3:4-dihydroxyphenanthraquinone), which dyes deep violet shades on alum mordant and blue on chrome, although the 4:5-dihydroxy-derivative is not a mordant colouring matter.

The present paper records some experiments made with the object of preparing colouring matters from phenanthrene through phenanthraquinone. The investigation may be divided into three parts:

(A) *Attempts to Prepare New Hydroxy-derivatives.*

2-Hydroxy- and 2:7-dihydroxy-phenanthraquinone can be readily prepared from phenanthrene. Attempts were made to

introduce additional hydroxyl groups into these compounds by methods of great value in the alizarin series, namely, by the action of sulphuric acid and manganese dioxide and by the action of fuming sulphuric acid, but these experiments did not give results of value. Probably the phenanthraquinone molecule was decomposed by the oxidising action of manganese dioxide and sulphuric acid. Fuming sulphuric acid gave 2-*hydroxyphenanthraquinone-monosulphonic acid*, and apparently also a soluble sulphonic acid derivative of 2:7-dihydroxyphenanthraquinone. It seemed out of the question to fuse these products with potassium hydroxide in order to displace the sulphonic by hydroxyl groups, as apparently the phenanthraquinone molecule will not resist this treatment. Graebe (*Annalen*, 1873, **167**, 143) has recorded that phenanthraquinonedisulphonic acid on fusion with potassium hydroxide gives no substance like alizarin.

No definite product was obtained by heating 2:7-dinitrophenanthraquinone with fuming sulphuric acid and sulphur according to the method used in the preparation of anthracene-blue from 1:5-dinitroanthraquinone. The only new hydroxy-derivative prepared was 2:7-?-trihydroxyphenanthraquinone, obtained from 2:7-dihydroxyphenanthraquinone by acetylation, nitration, reduction, diazotisation, and boiling with water (P., 1913, **29**, 268). It gives a brown colour with potassium hydroxide, so that its dyeing properties are not very interesting. Judging from its colour it is probably 2:4:7-trihydroxyphenanthraquinone.

2:7-*Diacetylaminophenanthraquinone* was prepared with the idea that on its nitration the acetylamino-groups might direct the nitro-group into a more favourable position than happened on nitrating 2:7-diacetoxyphenanthraquinone, but up to the present this has not been tried.

(B) *Atttempts to Prepare Anilino-derivatives of Phenanthraquinone and Closely Related Compounds.*

Owing to the exclusion of methods of producing phenanthraquinone dyestuffs through the sulphonic acids, nitration or bromination seemed the inevitable first steps. It was found that a number of bromo-nitro-derivatives could be prepared by nitrating bromo-derivatives and vice versa. *Dibromonitro-* and *bromodinitro-phenanthraquinone* were prepared by nitrating the dibromophenanthraquinone obtained by brominating phenanthraquinone in nitrobenzene solution, and *bromo-2-nitro-* and *bromo-4-nitro-phenanthraquinone* were obtained by brominating the corresponding mononitro-compounds. In the anthraquinone series

bromine atoms are easily displaced by anilino-groups by Ullmann's method (*Ber.*, 1901, **34**, 2174), and in this treatment nitro-groups are apparently reduced or displaced by anilino-groups (D.R.-P., 113011); some of the anilino-derivatives of anthraquinone have interesting dyeing properties (for example, alizarin-cyanine-green, which is 1:4-di-*p*-toluidinoanthraquinonedisulphonic acid; see also D.R.-P., 113011, 121155, 142512, etc.).

Led by these considerations to apply the same method to the bromonitro-derivatives of phenanthraquinone, we have obtained 2:7-*dianilino-*, ?:?-*dianilino-*, 2-*nitroanilino-*, 4-*nitroanilino-*, *nitrodianilino-*, and *dinitroanilino-phenanthraquinone*. These are all dyes giving dark green, blue, or black shades on wool (Eng. Pat. 9311 of 1915). Sulphonic derivatives of dianilino- and 2-nitroanilino-phenanthraquinone have also been prepared. In several cases it was found that it was advantageous to dye on chrome-mordanted wool, although it was difficult to give any reason for this.

Bromo-p-*nitroanilinophenanthraquinone* was obtained by the action of *p*-nitroaniline on dibromophenanthraquinone, but it has no dyeing properties. Equally uninteresting as to its dyeing properties was *dibenzidinophenanthraquinone*, prepared from the same dibromo-compound by the action of benzidine.

(C) *Attempts to Prepare Phenanthraquinone Vat Dyes.*

2-*Benzoylamino-*, 2-*phthalylamino-*, 2-*oxalylamino-*, 2:7-*dibenzoyldiamino-*, and 2:7-*diphthalyldiamino-phenanthraquinone* have been prepared by the action of acid chlorides on the corresponding amino-compounds. They are all dissolved by alkaline hyposulphite and precipitated from the solution on oxidation; 2-benzoylaminophenanthraquinone dyes pale pink shades on cotton; the 2-phthalylamino-derivative gives pale yellow shades, and the benzoyl derivative from 2:7-diaminophenanthraquinone brownish-orange shades.

Attempts to prepare more complex vat dyes were not very successful. A black product which dissolved in alkali hyposulphite was obtained by heating 2-aminophenanthraquinone with *p*-dibromobenzene in naphthalene solution in the presence of sodium acetate and copper chloride, but a pure substance was not isolated, nor could the brown product be purified which was obtained from dibromophenanthraquinone and 2-aminophenanthraquinone in the presence of sodium carbonate and copper oxide. An impure dye giving violet shades was prepared from dibromophenanthraquinone and *p*-phenylenediamine in nitrobenzene solu-

tion in the presence of copper chloride and fused sodium acetate. Dibromophenanthraquinone and β-naphthylamine in dimethylaniline solution in the presence of copper powder gave an impure, green substance. Almost colourless products were obtained on fusing 2:7-diaminophenanthraquinone with potassium hydroxide as in the preparation of indanthrene.

2:7-Diaminophenanthraquinone is deeply coloured, but apparently its dyeing properties had not been tested, it being too insoluble in all ordinary solvents. It dissolves, however, in alkaline sodium hyposulphite solution with a pale yellow colour, and is reprecipitated on oxidation, but the leuco-compound does not seem to possess any affinity for wool. Its *monosulphonic acid* was prepared, and dyed dull green shades on alum-mordanted wool. That dyestuffs can be prepared by coupling diazotised 2:7-diaminophenanthraquinone with phenolic substances had been already shown by Litthauer (*Ber.*, 1893, **26**, 848), but he did not crystallise his products and only described them very briefly.. We have obtained crystalline *phenanthraquinone-2:7-bisazophenol.* It dissolves in potassium hydroxide with a brown colour, and hence was not further examined.

Experimental.

Barium 2-Hydroxyphenanthraquinonesulphonate, $C_{14}H_6O_6SBa$.

Fifteen grams of fuming sulphuric acid (SO_3 = 70 per cent.) were added to 1·5 grams of 2-hydroxyphenanthraquinone in a small stoppered bottle, which was kept closed at 35—40° for forty-eight hours. The product was then poured into 300 c.c. of water, when a deep red solution was obtained which gave no precipitate on boiling, as in the case of the preparation of alizarin-Bordeaux. To this solution was added excess of barium carbonate, the whole boiled and filtered, and the residue thrice boiled with 300 c.c. of water and filtered. The collected filtrate was allowed to remain in a tall cylinder for one day in order that the barium carbonate that passed through the filter-paper might settle down. The filtrate was of a reddish-violet colour, which turned to deep violet on concentration. The whole of the filtrate was evaporated to dryness. A violet substance was thus obtained, which was dissolved and reprecipitated from water, which process was thrice repeated in order to obtain the substance in a pure state. It dissolves readily in boiling water, but is quite insoluble in absolute alcohol. The substance was dried at 140° for one hour and analysed:

0·2512 gave 0·1263 $BaSO_4$. S = 6·91.
0·1305 „ 0·0713 $BaSO_4$. Ba = 32·13.
$C_{14}H_6O_6SBa$ requires S = 7·29; Ba = 31 21 per cent.

Nitro-2:7-*diacetoxyphenanthraquinone*, $C_{14}H_5O_2(OAc)_2 \cdot NO_2$.

Three grams of 2:7-diacetoxyphenanthraquinone were added to 30 c.c. of cold nitric acid (D 1·39), and the mixture was warmed at 50—60° for one and a half minutes by plunging the containing vessel into boiling water. The mixture was then at once poured into water, and the nitro-compound, which was precipitated as a sandy, yellowish-brown powder, was crystallised from a mixture of acetic acid and acetone, and obtained in yellowish-brown, rhombic prisms which did not melt below 290°:

0·1100 gave 0·2367 CO_2 and 0·0307 H_2O. C = 58·70; H = 3·10.
0·1786 „ 6·2 c.c. N_2 (moist) at 24° and 758 mm. N = 3·98.
$C_{18}H_{11}O_8N$ requires C = 58·53; H = 2·98; N = 3·79 per cent.

Nitro-2:7-*dihydroxyphenanthraquinone*, $C_{14}H_5O_2(OH)_2 \cdot NO_2$.

The above acetyl derivative was hydrolysed by boiling for a short time with glacial acetic acid and a few drops of concentrated sulphuric acid. On adding excess of boiling water to the mixture, the nitrodihydroxy-compound was precipitated as a brown powder which did not melt below 290°:

0·1215 gave 0·2628 CO_2 and 0·0284 H_2O. C = 59·00; H = 2·60.
0·1423 „ 6·4 c.c. N_2 (moist) at 30° and 757 mm. N = 5·10.
$C_{14}H_7O_6N$ requires C = 58·93; H = 2·45; N = 4·91 per cent.

Amino-2:7-*dihydroxyphenanthraquinone*, $C_{14}H_5O_2(OH)_2 \cdot NH_2$.

One gram of nitrodiacetoxyphenanthraquinone was heated on the water-bath with 2 grams of finely granulated tin and 15 c.c. of concentrated hydrochloric acid until all the tin had dissolved. The yellowish-brown nitro-compound did not dissolve, but turned at first deep brown and then became of a much paler brown colour. This pale brown, insoluble substance was collected and warmed with aqueous ferric chloride solution, when its colour became much deeper. It was finally boiled with dilute hydrochloric acid until free from inorganic matter, collected, and washed with water. The aminodihydroxy-compound thus obtained is a deep brown substance consisting of small, rectangular plates. It does not melt below 290°, is insoluble in all ordinary organic solvents, but dissolves in alkali hydroxide with a brown colour:

0·1210 gave 0·2897 CO_2 and 0·0403 H_2O. C = 65·29; H = 3·70.
$C_{14}H_9O_4N$ requires C = 65·88; H = 3·53 per cent.

Acetylamino-2:7-diacetoxyphenanthraquinone, $C_{14}H_5O_2(OAc)_2 \cdot NHAc$.

This was obtained by acetylating the preceding compound by boiling with acetic anhydride and a drop of pyridine. It was precipitated by adding alcohol to the acetylation mixture. It could not be crystallised, and did not melt below 295°:

0·1232 gave 0·2824 CO_2 and 0·0459 H_2O. C = 62·52; H = 4·15.
$C_{20}H_{15}O_7N$ requires C = 62·99; H = 3·93 per cent.

2:7:?-*Trihydroxyphenanthraquinone*, $C_{14}H_5O_2(OH)_3$.

The aminohydroxy-compound was suspended in ice-cold 10 per cent. sulphuric acid and diazotised with the calculated amount of sodium nitrite. It dissolved almost entirely. The solution was filtered and boiled, when the trihydroxyphenanthraquinone was precipitated as a reddish-brown substance which did not melt below 290°; it can be dissolved in pyridine and precipitated by alcohol, and dissolves in alkali with a brown colour:

0·1236 gave 0·2951 CO_2 and 0·0368 H_2O. C = 65·11; H = 3·31.
$C_{14}H_8O_5$ requires C = 65·62; H = 3·12 per cent.

2:7:?-*Triacetoxyphenanthraquinone*, $C_{14}H_5O_2(OAc)_3$.

This was obtained by acetylating 2:7:?-trihydroxyphenanthraquinone with acetic anhydride and a trace of pyridine. It was precipitated by alcohol from the solution in acetic anhydride, and was then recrystallised from glacial acetic acid, being obtained as a reddish-brown, microcrystalline powder melting at about 280°:

0·1130 gave 0·2590 CO_2 and 0·0373 H_2O. C = 62·51; H = 3·67.
$C_{20}H_{14}O_8$ requires C = 62·83; H = 3·66 per cent.

2:7-*Diacetylaminophenanthraquinone*, $C_{14}H_6O_2(NHAc)_2$.

One gram of 2:7-diaminophenanthraquinone was heated with 1 gram of fused sodium acetate and 8 c.c. of acetic anhydride in a sealed tube at 160° for one hour. The contents of the tube were mixed with an equal volume of glacial acetic acid and poured into water. The precipitated acetyl compound was recrystallised twice from a mixture of acetic acid and alcohol. It is a chocolate-brown substance which does not melt below 295°, is readily soluble in acetic acid, and sparingly so in alcohol:

0·1150 gave 0·2821 CO_2 and 0·0450 H_2O. C = 66·90; H = 4·35.
0·1255 „ 9·5 c.c. N_2 (moist) at 30° and 758 mm. N = 8·53.
$C_{18}H_{14}O_4N_2$ requires C = 67·08; H = 4·31; N = 8·69 per cent.

Dibromonitrophenanthraquinone, $C_{14}H_5O_2Br_2 \cdot NO_2$.

Dibromophenanthraquinone (1 gram), obtained by brominating phenanthraquinone in nitrobenzene solution (D.R.-P., 222206), was boiled with nitric acid (35 c.c.; D 1·42) for half an hour and the solution poured into water. The new substance was deposited as a yellow precipitate, which crystallised from acetic acid in yellow, prismatic needles melting at 244—245°:

0·1644 gave 4·6 c.c. N_2 at 28° and 762 mm. N = 3·19.

$C_{14}H_5O_4NBr_2$ requires N = 3·40 per cent.

Bromodinitrophenanthraquinone, $C_{14}H_5O_2Br(NO_2)_2$.

A mixture of dibromophenanthraquinone (1 gram), fuming nitric acid (10 c.c.; D 1·51), and concentrated sulphuric acid (1·5 c.c.) was boiled for two minutes and the solution poured into water. The yellow precipitate crystallised from a mixture of acetic acid (2 parts) and nitrobenzene (1 part) in yellow, prismatic needles melting above 300°:

0·1530 gave 10 c.c. N_2 at 28° and 764 mm. N = 7·49.

$C_{14}H_5O_6N_2Br$ requires N = 7·43 per cent.

Bromo-2-nitrophenanthraquinone, $C_{14}H_6O_2Br \cdot NO_2$.

2-Nitrophenanthraquinone (1 gram), bromine (0·6 c.c.), and acetic acid (6 c.c.) were heated together in a sealed tube at about 140° for two hours. Shining, reddish-yellow plates, which were deposited in the tube, were washed out with acetic acid, collected, and washed with alcohol. The substance can be recrystallised from nitrobenzene, and melts above 300°:

0·1693 gave 6·5 c.c. N_2 at 25° and 763 mm. N = 4·42.

$C_{14}H_6O_4NBr$ requires N = 4·22 per cent.

Bromo-4-nitrophenanthraquinone, $C_{14}H_6O_2Br \cdot NO_2$.

One gram of 4-nitrophenanthraquinone was dissolved in as little nitrobenzene as possible at 110°, excess of bromine added, and the heating continued at the same temperature for one and a half hours. On cooling, the new substance was deposited in yellow prisms, which, when recrystallised from acetic acid, melted at 224—226°:

0·1501 gave 6 c.c. N_2 at 23° and 760 mm. N = 4·62.

$C_{14}H_6O_4NBr$ requires N = 4·22 per cent.

2:7-*Dianilinophenanthraquinone*, $C_{14}H_6O_2(NHPh)_2$.

A mixture of 2:7-dibromophenanthraquinone (1 gram), aniline (10 grams), and copper powder (0·25 gram) were boiled together for two and a half to three hours. The solution was then filtered hot and poured into excess of dilute hydrochloric acid, when the dianilinophenanthraquinone was precipitated. It was collected and purified by dissolving in a mixture of nitrobenzene and acetic acid and slowly precipitating with ether, when it was obtained as a non-crystalline, blue-black precipitate. It dyes mordanted or unmordanted wool in blue-black shades, and does not melt below 300°:

0·1050 gave 7 c.c. N_2 at 32° and 760 mm. N = 7·49.
$C_{26}H_{18}O_2N_2$ requires N = 7·18 per cent.

?:?-*Dianilinophenanthraquinone*, $C_{14}H_6O_2(NHPh)_2$.

Dibromophenanthraquinone (D.R.-P., 222206) was boiled with aniline and copper powder in the same proportions as in the preceding case for the same length of time, and the substance isolated and purified in the same way. In this case, also, the substance could not be obtained crystalline. It is a bluish solid, which dyes chrome-mordanted or unmordanted wool in greenish-blue shades and does not melt below 300°:

0·1436 gave 9·4 c.c. of N_2 at 27° and 760 mm. N = 7·42.
$C_{26}H_{18}O_2N_2$ requires N = 7·18 per cent.

2-*Nitroanilinophenanthraquinone*, $C_{14}H_6O_2(NO_2)\cdot NHPh$.

This was prepared exactly in the above way from bromo-2-nitrophenanthraquinone. It is a blue-black substance, and dyes chrome-mordanted or unmordanted wool in fine, blue-black shades and does not melt below 300°:

0·1102 gave 0·2836 CO_2 and 0·0388 H_2O. C = 70·19; H = 3·91.
0·1089 „ 7·8 c.c. N_2 at 25° and 762 mm. N = 8·26.
$C_{20}H_{12}O_4N_2$ requires C = 69·77; H = 3·49; N = 8·14 per cent.

4-*Nitroanilinophenanthraquinone*, $C_{14}H_6O_2(NO_2)\cdot NHPh$.

This was prepared in the same way from bromo-4-nitrophenanthraquinone. It is a black, amorphous solid, which dyes wool in blackish shades and does not melt at 300°:

0·1200 gave 8·9 c.c. N_2 at 30° and 760 mm. N = 8·40.
$C_{20}H_{12}O_4N_2$ requires N = 8·14 per cent.

Nitrodianilinophenanthraquinone, $C_{14}H_5O_2(NO_2)(NHPh)_2$.

This was prepared exactly as above from dibromonitrophenanthraquinone. It dyes wool in black shades:

0·1012 gave 8·45 c.c. N_2 at 32° and 758 mm. N = 9·37.

$C_{26}H_7O_4N_3$ requires N = 9·66 per cent.

Dinitroanilinophenanthraquinone, $C_{14}H_5O_2(NO_2)_2{\cdot}NHPh$.

This was obtained in the same way by the action of aniline on bromodinitrophenanthraquinone in the presence of copper powder. It is a black powder, and gives greenish-black shades on wool:

0·1128 gave 10·8 c.c. N_2 at 30° and 758 mm. N = 10·80.

$C_{20}H_{11}O_6N_3$ requires N = 10·79 per cent.

Dianilinophenanthraquinonesulphonic Acid.

One part of dry dianilinophenanthraquinone was heated with ten parts of sulphuric acid (D 1·84) at 110—120° for one hour. The product was poured into water, boiled and filtered, and the sulphonated dyestuff salted out from the cold filtrate. It dyes greener shades than the parent substance, and the dyeings are faster to light.

2-Nitroanilinophenanthraquinonesulphonic Acid.

One part of dry 2-nitroanilinophenanthraquinone was heated with ten parts of sulphuric acid (D 1·84) at 125—130° for two hours, and the product poured into water, when the sulphonated substance was precipitated. It can be dissolved in a large amount of boiling water, from which it separates on cooling, and can also be most conveniently salted out. It dyes chrome-mordanted wool in olive green shades.

Bromo-p-nitroanilinophenanthraquinone, $C_{14}H_6O_2Br{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$.

Dibromophenanthraquinone (1 gram), *p*-nitroaniline (1 gram), dimethylaniline (5 c.c.), and a trace of copper powder were heated together at 160° for three and a half hours. The product was poured into dilute hydrochloric acid, when the new substance was precipitated. It was purified by dissolving in acetone and precipitating with ether, when it was obtained as a reddish-violet substance, which did not melt at 280°. It does not dye wool:

0·1132 gave 6·2 c.c. N_2 at 32° and 759 mm. N = 6·15.

$C_{20}H_{11}O_4N_2Br$ requires N = 6·62 per cent.

Dibenzidinophenanthraquinone, $C_{14}H_6O_2(NH{\cdot}C_{12}H_8{\cdot}NH_2)_2$.

A mixture of dibromophenanthraquinone (1 gram), benzidine (1·5 grams), fused sodium acetate (2 grams), cupric chloride (0·35 gram), and nitrobenzene (20 grams) was heated to boiling for two hours. On cooling, ether was added to the solution to precipitate the new substance, which was collected and washed with alcohol. It was then boiled with water to free it from any inorganic impurity. It is a black powder which does not melt and does not dye wool:

0·1310 gave 12 c.c. N_2 at 30° and 758 mm. N = 10·34.
$C_{38}H_{28}O_2N_4$ requires N = 9·80 per cent.

2-*Benzoylaminophenanthraquinone*, $C_{14}H_7O_2{\cdot}NHBz$.

Half a gram of 2-aminophenanthraquinone was dissolved in 20 c.c. of nitrobenzene, and 2 c.c. of benzoyl chloride were added to the solution. The mixture was heated at 100° for twenty minutes and allowed to cool, when needle-shaped crystals of the new substance were deposited. When crystallised from nitrobenzene it consists of fine, pinkish, needle-shaped crystals melting at 295°. It is a vat dye, and dyes cotton in pale pink shades:

0·1591 gave 6·6 c.c. N_2 at 31° and 747 mm. N = 4·59.
$C_{21}H_{13}O_3N$ requires N = 4·28 per cent.

2-*Phthalylaminophenanthraquinone*, $C_6H_4(CO{\cdot}NH{\cdot}C_{14}H_7O_2)_2$.

A solution of phthalyl chloride (2·5 grams) and 2-aminophenanthraquinone (0·5 gram) in nitrobenzene (20 c.c.) was heated for two hours at 100—105°. On cooling the mixture, orange-coloured crystals of the new substance were deposited. It was collected, washed with alcohol, and recrystallised from nitrobenzene, when it was obtained in pale orange, needle-shaped crystals, which did not melt at 295°. It behaves as a vat dye and gives pale yellow shades on cotton:

0·1931 gave 8·2 c.c. N_2 at 29° and 748 mm. N = 4·75.
$C_{36}H_{20}O_6N$ requires N = 4·86 per cent.

2-*Oxalylaminophenanthraquinone*, $(CO{\cdot}NH{\cdot}C_{14}H_7O_2)_2$.

Oxalyl chloride (1·5 c.c.) was added to a solution of 0·5 gram of 2-aminophenanthraquinone in 20 c.c. of nitrobenzene, and the solution heated at 80—90° for two hours. A crystalline mass was

formed, which was collected, washed with alcohol, and recrystallised from nitrobenzene, from which it was deposited in clusters of reddish-brown needles. The substance does not melt at 295°. It dissolves in an alkaline solution of sodium hyposulphite and is reprecipitated on oxidation, but is not absorbed from the vat by cotton:

0·1484 gave 6·85 c.c. N_2 at 30° and 753 mm. N = 5·31.
$C_{30}H_{16}O_6N_2$ requires N = 5·60 per cent.

2:7-*Dibenzoyldiaminophenanthraquinone*, $C_{14}H_6O_2(NHBz)_2$.

To a solution of 2:7-diaminophenanthraquinone (0·5 gram) in 10 c.c. of boiling nitrobenzene 2 c.c. of benzoyl chloride were added, and the mixture was boiled for half an hour under a reflux condenser. On cooling, the substance was deposited in large needles. When recrystallised from nitrobenzene it forms brick-red needles, which do not melt at 295°. It behaves like a vat dye, giving brownish-orange shades on cotton:

0·0955 gave 5·2 c.c. N_2 at 28° and 760 mm. N = 6·20.
$C_{28}H_{18}O_4N_2$ requires N = 6·28 per cent.

2:7-*Diphthalyldiaminophenanthraquinone*,

$$C_6H_4\begin{matrix}<\text{CO·NH·C}_{14}\text{H}_6\text{O}_2\text{·NH·CO}\\ \text{CO·NH·C}_{14}\text{H}_6\text{O}_2\text{·NH·CO}>\end{matrix}C_6H_4.$$

A mixture of 2:7-diaminophenanthraquinone (0·5 gram), dissolved in nitrobenzene (15 c.c.), and phthalyl chloride (1 c.c.) was boiled under a reflux condenser for half an hour, and the solution filtered hot. On cooling, a brick-red precipitate was obtained, which crystallised from nitrobenzene in circular needle clusters. It does not melt at 295°. It dissolves in alkaline hyposulphite and is reprecipitated from the solution on oxidation, but is not absorbed from the vat by cotton:

0·1220 gave 8·1 c.c. N_2 at 22° and 761 mm. N = 7·72.
$C_{44}H_{24}O_8N_4$ requires N = 7·61 per cent.

2:7-*Diaminophenanthraquinonesulphonic Acid*,
$C_{14}H_5O_2(NH_2)_2\text{·}SO_3H$.

An excess of fuming sulphuric acid (SO_3 = 70 per cent.) was mixed with 2:7-diaminophenanthraquinone in a bottle, when much heat was generated. The bottle was kept closed for forty-eight hours, after which the mixture was poured into water, when

the sulphonic acid was precipitated. The substance is insoluble in most organic solvents, but is sparingly soluble in alkali hydroxide. In the moist state it dyes alum-mordanted wool in dull green shades:

0·2222 gave 16·7 c.c. N_2 at 32° and 760 mm. N = 8·36.
$C_{14}H_{10}O_5N_2S,H_2O$ requires N = 8·80 per cent.

Phenanthraquinone-2:7-bisazophenol, $C_{14}H_6O_2(N{:}N{\cdot}C_6H_4{\cdot}OH)_2$.

One gram of 2:7-diaminophenanthraquinone was suspended in 5 per cent. sulphuric acid and diazotised by adding 0·58 gram of sodium nitrite. The solution of the diazo-compound was added to a solution of phenol, and the whole carefully rendered alkaline by sodium carbonate. The mixture was then acidified, and the insoluble substance collected and crystallised from a mixture of alcohol and nitrobenzene. It was obtained in brown, lenticular crystals, which did not melt at 295° and dissolved in alkali with a brown colour:

0·1134 gave 0·2890 CO_2 and 0·0367 H_2O. C = 69·51; H = 3·60.
0·1511 „ 16·0 c.c. N_2 (moist) at 25° and 759 mm. N = 12·21.
$C_{26}H_{16}O_4N_4$ requires C = 69·64; H = 3·57; N = 12·50 per cent.

Phenanthraquinone-2:7-bisazophenyl Acetate,
$C_{14}H_6O_2(N{:}N{\cdot}C_6H_4{\cdot}OAc)_2$.

The preceding compound was acetylated by boiling with acetic anhydride and a drop of pyridine. On adding alcohol to the mixture, the acetyl derivative was precipitated; this crystallised from acetic acid in brick-red, rhombic prisms melting at 274°:

0·1660 gave 0·4126 CO_2 and 0·0589 H_2O. C = 67·84; H = 3·94.
0·2390 „ 21·8 c.c. N_2 (moist) at 25° and 761 mm. N = 10·46.
$C_{30}H_{20}O_6N_4$ requires C = 67·67; H = 3·76; N = 10·52 per cent.

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Newer Standpoints in the Study of Nutrition.

A Lecture Delivered before the Chemical Society on May 18th, 1916.

By Frederick Gowland Hopkins.

An invitation to lecture before the Chemical Society is for me a great personal honour. I feel, moreover, as a professed biochemist, much gratification from the circumstance that one of my calling has been chosen for the honour. It is, indeed, a source of no small satisfaction to those who have to apply chemistry to the animal to feel that during recent years the pure chemist has displayed a growing sympathy with that particular application of the science. A few years ago the sympathy was, frankly, less.

Properly to appreciate any branch of inquiry one must fully understand its aims, and, by experience or otherwise, one must have obtained faith in its methods. Now, in the application of chemistry to medicine and physiology, both aims and methods are more remote from the every-day thoughts and occupations of the pure chemist than in any other branch of inquiry to which his science is applied. This is, of course, only true when the living animal body is itself being dealt with; not when its foods, its constituents, or its products are under study in the laboratory; but it is only as a branch of science directly concerned with the animal that biochemistry can claim to be a separate discipline deserving of a special name. A certain sense of remoteness was, I think, the sufficient cause for the circumstance that the biochemist used to feel at some disadvantage when addressing an audience of those who profess the pure science.

Now, however, and especially this evening, I feel that I can count upon your sympathy, even though I have selected for my address a somewhat special and limited—though not, I think, unimportant—aspect of my subject. I am sure you will appreciate the aims of the inquiry with which I shall deal, and I hope you will have some faith in the methods used.

I propose to discuss, on certain special and limited lines, the fate of protein nutriment as it is dealt with in the animal body.

Any attempt to study this very fundamental aspect of nutrition from clear chemical points of view seemed, twenty years ago, to be almost hopeless. At that time, our knowledge of the chemistry of proteins was, of course, very incomplete, and the student of metabolism owes a heavy debt to the chemical labours which during recent years have done so much to throw light on the constitution of the protein molecule. This debt is largely—but by no means

so exclusively as some people seem to think—due to Emil Fischer and his co-workers.

The chemical knowledge of proteins which we now possess is sufficient to increase very greatly our understanding of the processes which occur in the animal. It required, however, an advance on the physiological side—the discovery of a peculiarity in metabolism which to the biochemist represents a very fortunate aspect of affairs—before the prospect for experimental study could be so favourable as we may now claim it to be.

If molecular reconstructions, oxidations, and the other more significant chemical events which occur in nitrogenous metabolism were wholly, or in the main, initiated in the intact molecule of protein itself, the complexity of this, and the consequent complexity of, at any rate, all the earlier products of change, would still leave the chemical investigator with a task of extreme difficulty. The advance on the physiological side, to which I have just referred, has made it clear, however, that complete hydrolysis precedes other processes of change. The complex protein molecule is dissected before it is used, whether for reconstruction, for supplying energy, or for other essential purposes. The animal body makes play with the constituent amino-acids of protein, and these are substances with clear-cut chemical properties based upon known molecular constitution.

It is scarcely necessary to remind you that on hydrolysis a typical protein breaks down, by resolution of the polypeptide linkings in its molecule, into an assembly of α-amino-acids of which some eighteen are known. We may not yet know all of them, but there is a good deal of evidence to show that we do know nearly all, and of those which have been separated, the constitution is for the most part fully known. There is no need for me to assemble the molecular formulæ of all these units before you; they are too familiar. There is so much significance, however, in the diversity of molecular structure which obtains among them, that I venture here to remind you of that diversity. You will remember that a number of them are aliphatic substances of various types: monocarboxylic and dicarboxylic acids; monoamino- and diamino-derivatives; some containing straight chains, others branched. One is a thio-compound, another contains the guanidine grouping. A number, on the other hand, are aromatic compounds, some being monocyclic, others heterocyclic; the benzene, the indole, and iminazole (glyoxaline) ring having each one or more representatives. The more clear the evidence that in metabolism the body deals with individual amino-acids, the more significant does this diversity become. The fate of an organic substance in a given

chemical milieu depends primarily upon its own molecular structure, and even amid the chemical complexities of the body properties due to such structure must still assert themselves. Substances so diverse must suffer diverse fates. The katabolism of protein follows not one line, but many lines. It is important, indeed, to realise that when we eat any individual protein, we are in effect taking into ourselves, not one substance, but well-nigh twenty substances, each possessing its own significance—sometimes greater, sometimes less—in the processes of nutrition.

I wish, therefore, to put before you very briefly, but as clearly as possible, the evidence upon which is based our present belief that before the proper metabolism of protein begins, its constituent amino-acids are liberated. This part of my subject will be familiar to many here. It may not be so to all, however, and it is essential to the development of my main exposition that the evidence referred to should be weighed, and, I hope, accepted.

I must deal first with evidence concerning the dealings of the body with a supply of new protein—with the proteins of its food. Later I will refer to the fate of the protein which has already formed part of the living tissues in so far as this is metabolised. The first thesis for which I will discuss the experimental support is this: that during digestion free amino-acids, and not complex polypeptide compounds, enter the blood from the intestine; in other words, that the digestion of proteins in the alimentary tract is a case of complete hydrolysis.

For this belief, we have first of all some indirect evidence of a very interesting sort: I mean the fact that the animal may display quite normal nutrition when depending on protein which has been totally hydrolysed before it is eaten. When a mixture of all the free amino-acids obtainable from protein has entirely replaced the normal intact protein of their food, an adult animal maintains itself, and a young animal grows. The experimental proof of this fact is abundant. It began at the hands of Otto Loewi in 1902. Various other workers have carried the proof further, and Abderhalden has accumulated evidence which is almost in excess of what is required for conviction. I will mention only one actual experiment, the last published by Abderhalden in this connexion. The material fed to the animal in this experiment was so thoroughly predigested as to contain no trace of any intact polypeptide compound whatever, as proved by conclusive tests. Nothing was present but the mixture of free amino-acids which results from complete artificial digestion. On this mixture as its sole nitrogenous supply a dog lived in good health for one hundred days. During this period the animal gained 10 kilos. in body-

weight, and when the experiment closed, there was nothing to suggest that it might not have been continued indefinitely. Such a result is convincing enough, and, as I have implied, the fact thus proved has become a commonplace among students of nutrition. I have myself seen scores of young animals grow steadily during experimental periods when no trace of intact protein, and no other source of flesh-forming material save free amino-acids, was passing their mouths.

There is, then, abundant proof of the capacity of the animal to synthetise its tissue proteins from free amino-acids when they are eaten, and to maintain itself quite satisfactorily on them; but this, you are entitled to say, is no direct proof that it *normally* absorbs free acids and not more complex protein derivatives from its bowel. I would urge, however, that it is at least very suggestive evidence even for this. The animal has, we know, wonderful powers of adaptation, but the synthesis of its tissue proteins from the medley of free amino-compounds calls for elaborate chemical adjustments, and the fact that it is accomplished with ease under the experimental conditions described suggests that the tissues are normally adjusted to the task, and that the process is always in action.

We have, however, direct evidence that it is the unconjugated acids which enter the blood from the bowel, and a proof that these, rather than elaborate complexes, arrive at the seats of utilisation in the living tissues. I must not attempt to deal with this evidence historically or more than briefly. The work of many investigators has contributed to it. I will refer only to such observations as seem to offer the most conclusive proof, and in which I have the faith which comes from personal repetition.

Posed with the question: What precisely enters the blood during the digestion of protein? the physiologist has for various reasons failed to get a really satisfactory answer by directing his observations to the progressive changes in the intestinal contents. Success has come rather by examination of the blood and tissues before and during a meal. Since, however, such questions must be put to the living (though anæsthetised) animal, the inquirer must expect to have to work on very small quantities of blood. That is his first limitation; one that makes him welcome micro-chemical methods whenever they are of proved accuracy. Another thing that the inquirer must recognise in advance is that nitrogenous metabolism is a rapid affair, especially in its early stages, and the products of digestion, once they have entered the cycle of change, are not likely to minister to his convenience by greatly accumulating anywhere. Actual separation of the products in

quantitative studies is scarcely to be hoped for. Abderhalden has, it is true, by working on very large quantities of blood, shown directly that much of the non-protein nitrogen present in the blood of animals during digestion is contained in free amino-acids, and several of these he obtained in the pure state for identification, but his evidence was qualitative only. For a quantitative method of measuring variations, we must be content with something less direct.

Now it will be known to many that an American worker, D. D. van Slyke, has so perfected the technique for liberating nitrogen from the amino-groups of free amino-acids by means of nitrous acid, that intelligent quantitative applications of the process have advanced our knowledge both of the constitution of proteins and of certain aspects of their metabolism. Four years ago, in conjunction with G. M. Meyer, he began to apply the method to the problem before us, and he has attained to what is, in my opinion, real success in solving it. From the polypeptide linkings, in which the amino-groups of the constituent amino-acids are engaged, nitrous acid liberates no nitrogen; only a little comes off, therefore, from polypeptides which have more than a compartively small molecular weight. The method measures free amino-groups, and an informed use of it will distinguish between free amino-acids and all other nitrogenous constituents of the tissues, so as to give a satisfactory measure of the nitrogen contained in the former alone.

The results obtained by van Slyke, on applying the method to the blood and tissues of the living animal, before and during digestion, will bring conviction to those who carefully consider them, and still more to those who care to obtain them for themselves. They show that it is mainly, if not entirely, in the form of free amino-acids, and not in complex associations of these, that our nitrogenous food begins its proper metabolism. In this form it reaches the tissues, to be dealt with according to their necessities.

As a matter of fact, our present belief that nitrogen is transported from gut to tissue, and from one tissue to another, not in protein complexes, but in the comparatively small molecules which result upon the complete hydrolysis of protein, is based, not alone on the kind of evidence already discussed, but also upon a variety of considerations all pointing in the same direction. We know, to mention but a few of them, that proteins foreign to the body, such as those contained in the food we eat, induce, if introduced while intact into the blood, a remarkable set of reactions which certainly do not follow on the normal ingestion of food. We know that the more complex polypeptides (the

albumoses and peptones) which result at the first stage of digestion, prove themselves foreign to the organism, if for no other reason than that, on entering the blood, they are promptly excreted in the urine. On the other hand, we know that free amino-acids, when they enter the blood at a normal rate, are promptly and normally metabolised.

In the starving animal, or in the animal with a food supply not equal to its needs, there is, of necessity, a mobilisation of the protein which has been previously built up in the tissues by condensation of circulating amino-acids. Tissues which are less essential to the vital functions of the body yield nitrogenous material to the organs which are associated with such urgent functions. In this case, also, there is scarcely a doubt that complete hydrolysis precedes all transport from one locality to another. For an understanding of this fact we have long been prepared by our knowledge of the proteoclastic enzymes (the autolytic ferments) found in living tissues, and of the factors which condition their activity. A study of the blood during abstinence is confirmative. We do not, for instance, find the specific proteins of muscle appearing in the blood when in starvation the muscles waste. We find no complex polypeptides of any kind, but we do find a supply of amino-acids always circulating; and since these are continually being metabolised, the supply can only be maintained by disintegration of the tissue proteins.

If the liberation of free amino-acids in digestion and in tissue autolysis were connected only with transport; if the reconstruction of chemically vague complexes in this or that organ always preceded the occurrence of deep-seated and significant processes in metabolism, there would not be so much immediate promise for the application of genuine chemical knowledge to the study of metabolism as certainly exists. We may assert, however, that in metabolism it is comparatively small molecules of known or ascertainable structure that undergo the most significant changes. I will return to the support of this claim later. You will, I think, appreciate both its reality and its importance rather better when certain other facts are before you, the facts which it is the immediate purpose of this lecture to disclose.

Although all students of nutrition have been impressed by the inherent interest and importance of the circumstance that the animal can maintain itself satisfactorily on a mixture of free amino-acids, I am not sure that it is fully recognised how excellent an opportunity for discriminating study of an important side of metabolism it has put into our hands. Since the animal flourishes on a mixture which can be fractionated, we are at once able, for

example, to determine what is the effect on growth and health of withdrawing this or that individual amino-acid from the supply. We can see whether, in any particular case, their withdrawal deprives the animal of something essential, or whether, perhaps, the removal from the food of any particular amino-acid under study may have little effect because the animal can synthesise it for itself or dispense with it altogether.

We can thus measure the relative nutritive importance of different molecular groups in the protein molecule. We may determine, again, how far one amino-acid is replaceable by another more or less closely related to it, and so test the limits of the capacity of metabolism to remodel a molecule of the kind. But we may hope to go further, and discover, by a more intimate study of the precise effects of its absence, whether a given amino-acid, already proved indispensable, possesses some special function—something other than what it contributes as a unit to the building-up of tissue protein—some function depending on its special molecular structure and not to be subserved by any of its congeners. We may ultimately be able to say what are the qualitative as well as the quantitative limitations to an efficient amino-acid supply, and what is the most harmonious balance of amino-acids for the nutrition of one animal species or another. Some of these points may be only of academic interest; others are certainly practical, and all are interesting. Having for control material an efficient nutritive mixture of known and comparatively simple substances derived from protein, we have the opportunity, on the above and other lines, of so altering the balance and harmony of the mixture as to throw much light on the intricacies of nutrition by protein; an opportunity which would certainly be absent if the animal body used as the raw material for its alchemy only the complex molecules of the intact proteins themselves.

Such a line of experimental study has still, of course, difficulties of its own. When protein has been hydrolysed, there are technical difficulties in connexion with the quantitative removal of some of the amino-acids from the mixture obtained. These will certainly be overcome, however, if the stimulus of interest in the subject prove sufficient. There will always be difficulties arising from the extreme adaptability to circumstances displayed by the living animal, which tends to obscure certain issues. But this adaptability has very definite limits, or there would be no science of nutrition. It is, after all, part of the essence of the problem to study and explain this adaptability, and, when necessary, in experimental studies, to learn how to elude its effects.

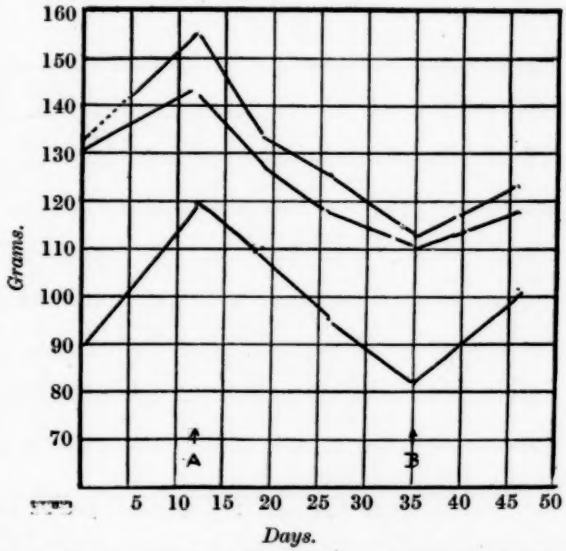
Some preliminary experiments on the lines just sketched I am

now to describe. They come mainly, but by no means exclusively, from my own laboratory. Most of them were carried out on animals no more noble than rats, and I am not sure whether I ought not in parenthesis to enter upon some defence of studies made on rats. The fundamentals of nutrition are the same in all mammals. Specific differences are displayed only in details which can always be controlled and allowed for. I would be as sure of finding facts observed from the physiological behaviour of rats confirmed in the human body as any won from the study of larger animals; sooner, indeed, than when the animal is one of the large ruminants of the farm. As a matter of fact, the rat offers exceptional advantages for the study of certain aspects of nutrition. Apart from the fact that it is omnivorous, its comparatively small demands have a great advantage when the experimental dietary requires much labour for its preparation. On the other hand, in special connexions, rats may with convenience be fed in large numbers, and statistical material thus obtained for the elimination of individual variations. Again, the small bodies of such animals are associated with so rapid a metabolism that indications of modified nutrition are quickly displayed. Last, and not least, we now possess, chiefly as the result of American work, extraordinarily accurate and very abundant data relating to the normal curve of growth and to other physiological constants of the rat. Needless to say, in nutritional experiments, as in all other experimental work, some preliminary knowledge of the peculiarities of one's material is a prime requisite for success. The rat, properly used, offers, as a matter of fact, highly standardisable material.

I will first put before you the body-weight curves of young rats to demonstrate the effect on the growth function of withdrawing this or that amino-acid from the food eaten. The diets which the animals were receiving comprised in all cases amino-acid mixtures combined with suitable amounts of filtered butter-fat or lard, potato starch, cane-sugar, and the requisite inorganic salts. In all the experiments which I shall deal with the diet was identical, except for the variation in the content of amino-acids. During the use of such synthetic diets, it is always essential to supply the at present mysterious vitamine or food hormone factor, which I myself, among others, have shown to be quite essential to growth. In the present experiments, this was supplied in the form of minute amounts of a nitrogen-free alcoholic extract of fresh milk. When the amino-acid mixture, which was always the sole source of nitrogen, comprised the whole assembly contained in a typical protein, growth was always maintained, and the rate of growth

on this diet usually served as the normal from which the effect of deficiencies was measured. The technique of preparing the amino-acid mixture was of the simplest. Casein was completely hydrolysed by forty hours' boiling with 25 per cent. sulphuric acid. The acid was removed and the solution of amino-acid evaporated to dryness. Acid hydrolysis destroys one amino-acid, and with completeness, one only. Tryptophan, which contains the indole nucleus, is wholly destroyed. Cystine is apparently partly destroyed. If to the products of acid hydrolysis the requisite amount (about 2 per cent. of the whole mixture) of tryptophan

FIG. 1.



Showing effect on growth of the presence or absence of tryptophan.

together with a little cystine be added, we obtain a product which satisfactorily supports growth.

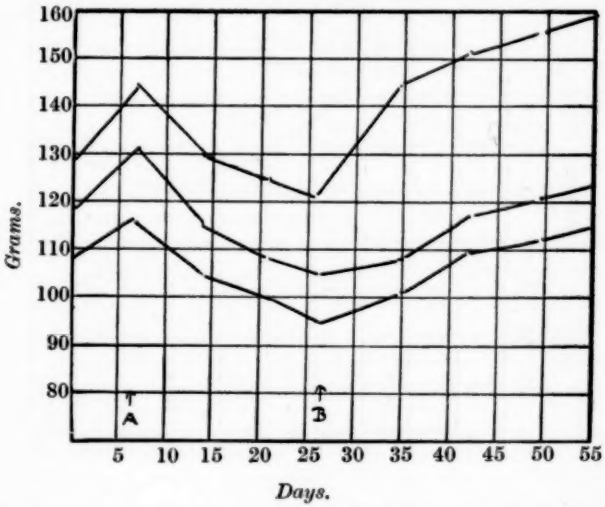
That a supply of tryptophan is necessary to the animal was first indicated by some work done by Miss Willcock (Mrs. Stanley Gardiner) and I, so far back as 1907. Abderhalden has since confirmed the fact on dogs. The circumstances just mentioned make it, I find, especially easy to prepare comparative dietaries showing the effect of the presence of absence of tryptophan. One has simply to add it or to refrain from adding it to the mixture obtained on acid hydrolysis, before making up the experimental dietary.

The curves of Fig. 1 bring out in a striking way the nutritive importance of tryptophan.

The first ascending part of the curve shows the growth of animals when on the whole amino-acid mixture. At the point *A* they were put on food from which tryptophan was absent. Loss of weight is seen to follow immediately, and if the animal is kept on such a diet, decline of weight continues and death follows, even though the consumption of food is, in the quantitative sense, more than sufficient for proper maintenance. On the other hand, growth will begin again if the tryptophan be restored before it is too late. This restorative effect is shown in the curve from the point *B* onwards.

It should be understood that the deficiency producing the loss

FIG. 2



At A *arginine and histidine were removed from the diet; at* B *they were restored.*

of weight exhibited in all the curves to be shown is always a qualitative and not a quantitative one. In none of the experiments put before you was the animal at any time eating less than enough to give it an efficient supply of energy.

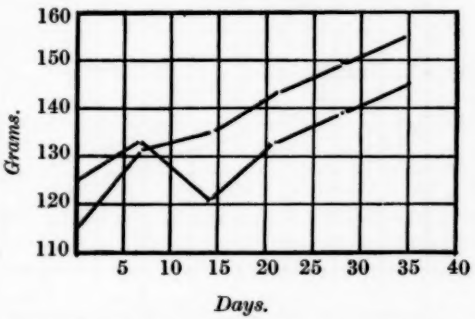
The need of a supply of tryptophan in the diet is urgent, as a great number of experiments have convinced me. The animal seems unable to synthetise the indole ring out of other materials. The necessary amount of tryptophan, however, is only about 30 milligrams a day in the case of an individual rat.

In the next curves (Fig. 2) is shown the effect on growth of quite another deficiency.

From the amino-acid mixture fed to the animals in the experiment which yielded this curve of body-weight, arginine and histidine were both removed by the method originally described by Kossel and Kutscher for the estimation of these two amino-acids. Why the deficiency was here made a double one will become clear a little later. As soon as these two complex amino-acids were removed from the diet, growth, as the curves show, gave place to loss of weight; on their restoration, growth began again.

It is evident, then, that the simultaneous removal from the normal amino-acid mixture of the units which contain the guanidine and iminazole groupings, greatly affects the nutrition of the animal. It needs these molecular groups, and is either unable to synthesise them from other material, or its synthetic powers cannot keep pace with its own normal demands.

FIG. 3.



Showing the growth in the absence of glutamic and aspartic acids. On the seventh day these acids were together removed from the food.

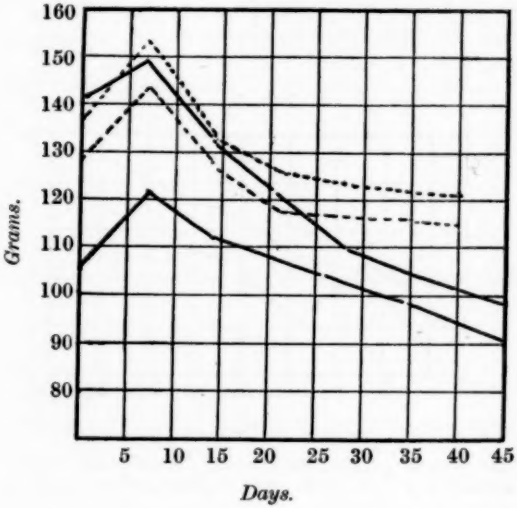
This may not be so in the case of other amino-acids, and would seem to be certainly otherwise in the case of some which possess a comparatively simple molecular structure. The following curves show that growth can occur in the absence of both glutamic and aspartic acids. F. W. Foreman has recently described a method for isolating these two acids from the mixture obtained on protein hydrolysis, and he himself removed them from the material which was used in the diet of animals exhibiting the growth shown in the curves of Fig. 3.

Now, in casein, glutamic and aspartic acids together constitute no less than some 28 per cent. of the weight of the molecule, and it is striking to see that by no means unsatisfactory growth was obtained in the absence of such prominent constituents of protein. One animal added 35 per cent. to its body-weight during a period

of four weeks. In such a case we are not, I think, to suppose that the process of new tissue formation dispenses with constituents which, like glutamic and aspartic acids, are normal to the proteins of the tissues. We have much evidence against this supposition. We are rather to believe that the simple straight chain aliphatic acids can, in the presence of ammonium salts, be synthetised from fat or carbohydrate derivatives by reactions possessed of sufficient velocity to maintain a supply for the purposes of growth.

The contrast between the effect of removing tryptophan, which constitutes only about $1\frac{1}{2}$ per cent. of the casein molecule, and

FIG. 4.



Continuous line, absence of tryptophan; dotted line, absence of arginine and histidine.

that of removing glutamic and aspartic acids, which constitute nearly 30 per cent., is sufficiently striking.

It is interesting to observe how curves of body-weight can demonstrate that, in the demand for amino-acids which seem essentially indispensable, there are, so to speak, degrees of urgency. The absence of one acid may, for example, cause a more rapid loss of weight than that of another. In Fig. 4 are curves which show once more the loss of weight which follows the absence of tryptophan, now compared with others showing the loss due to the absence of arginine and histidine.

In all cases (I have selected only a few out of many observations), the lack of the indole derivative produces the more marked

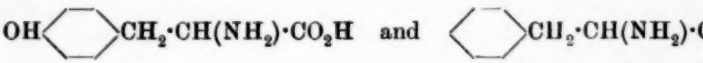
effect; loss of flesh is more rapid and continuous than when the guanidine and iminazole derivatives are concerned. This difference, like the other results that I am putting before you, can be obtained with great constancy. At the moment, we have not the data upon which to base an explanation of such a difference in this or in any similar case. It may depend only on the relative amounts of this or that acid, which tissue breakdown is capable of supplying in a given time. It is possible and more likely that such an amino-acid as tryptophan may be required for something other than structural purposes: that the indole nucleus, for instance, ministers to some dynamic function in the body of more urgent importance than any purpose subserved by, say, arginine and histidine. If so, we can understand how tissue breakdown would be the more rapid in order to maintain a supply for the more urgent demand. On the other hand, it is possible that the difference depends on factors which are more purely chemical. The animal body has much more extensive synthetic powers than used to be ascribed to it; but it has more limitations than the plant in this respect. The formation of the indole ring would seem, as I have said, to be beyond its powers. It cannot, at any rate, call on reactions for its production which have sufficient velocity. On the other hand, we have some grounds—chemical grounds, at least—for believing that the body may synthesise the iminazole ring, and, if so, because of a physiological relation to which I shall shortly allude, it may also improvise the guanidine complex. These two complexes, like others contained in protein, it normally receives, directly or indirectly, from the plant, by taking them in its food. With a failure in this supply, however, may come such an alteration in tissue equilibrium that reactions, always possible and imminent, or, more probably, always occurring to some small extent, proceed at an increased rate. Speaking teleologically, we might say that the living cells call up their chemical reserves. The normal position is not recaptured, but disaster is diverted or delayed. These are pure speculations, but one's indulgence in them is justified by other experimental facts, besides the one before us. I only mention them here to illustrate the kind of problem that arises in the course of a detailed study of nutrition; problems which are, in essence, chemical.*

Although, as I have emphasised, great diversity obtains among the amino-acids which arise during the digestion of protein, some of them are more or less closely related in respect of chemical

* It is possible that Kossel and Kutscher's method does not remove the last traces of arginine and histidine. I have been at some trouble to detect these amino-acids in the mixture as fed, but have failed to do so.

structure to certain others; and it would seem that such related acids may have some degree of equivalence in the processes of nutrition. With either, but not with both, of a given pair, the animal can, it would seem, more or less conveniently dispense.

As is well known, all typical proteins yield both tyrosine and phenylalanine:



which differ merely by the presence or absence of the phenol hydroxyl group.

Dr. G. Totani set himself in my laboratory to test whether or not tyrosine would prove to be an indispensable constituent of the nutritive amino-acid mixture. He was met by the difficulty that in this case there is no method available for rigorously removing all that substance from the assembly of acids. He fed animals, however, on material which, as careful study showed, contained no more than a very small remainder of that present in the original protein. On this he got satisfactory growth.

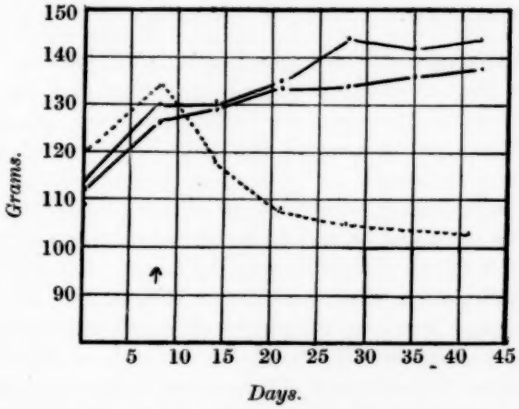
I think we may safely ascribe growth in the absence of tyrosine in part, at least, to the circumstance that the phenylalanine, which was still present in the food, is more or less equivalent to tyrosine, and can cover the essential demands of the animal. That tyrosine can be formed from phenylalanine in the body is known from the experiments of Embden, who showed that when the latter is perfused through a surviving liver, the former is produced. Dr. Totani's further results, however, furnish at least a suggestion that the animal can call up some power of synthesising the benzene ring. He fed other animals on the hydrolytic cleavage products of gelatin, which contains neither tyrosine nor tryptophan. On this, of course, there was complete failure of nutrition. Nothing, I think, could make you realise more fully why gelatin does not maintain the nutrition of man or animal than experiments like those I am putting before you. The entire absence of tryptophan from its molecule stamps it at once as a deficient food-stuff.

In Dr. Totani's experiments, the addition of tyrosine and tryptophan greatly improved the nutritive power of the gelatin products, as was to be expected; but what surprised us was the circumstance that many animals displayed fairly satisfactory growth after the addition of tryptophan alone; they grew, that is to say, in the absence of tyrosine and with an extraordinarily small supply of the equivalent phenylalanine. Now it must be admitted that gelatin may contain some unknown aromatic compound; we are, unfortunately, not quite sure on the point. If so, however, it is certainly present in very small amount, and there

seems, as I have said, to be a suggestion in Dr. Totani's results that the animal, while unable to produce the indole ring, has some power of synthesising the benzene ring in the course of making phenylalanine and tyrosine, which are certainly necessary for the formation of new tissue protein during growth.

I must now refer to another case of apparent equivalence between two amino-acids in metabolism; one which is of chemical as well as of physiological interest. It is a case which bears closely on other points raised in this lecture. We have seen how marked is the effect of removing arginine and histidine together. I will now show you curves of body-weight obtained when only one of the two is absent from the food. The lower curve of Fig 5 shows once more the rapid fall when both are lacking. The middle

FIG. 5.

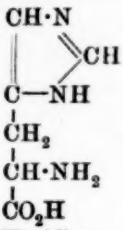


Dotted curve shows loss of body-weight when (on the 8th day) both arginine and histidine were removed from the diet. Upper curve shows the effect when, of the two, only histidine was present; middle curve with arginine alone.

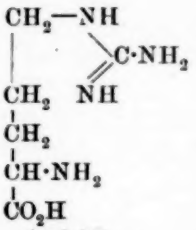
curve illustrates the change in body-weight when of the two histidine alone is absent; the upper curve shows the result obtained when histidine is given in the absence of arginine. Instead of a rapid loss of tissue, there is, when either is present alone, something more than maintenance; there is quite appreciable growth. As a matter of fact, in the particular experiment which yielded the curves shown, the amount of the amino-acid in question was in each case much smaller than that required to restore the balance of a normal amino-acid mixture. Better growth is obtained when either substance is given in amount equal to the normal sum of both as present in casein.

Either of these two protein constituents can, apparently, subserve the functions normally subserved by both together.

This is not surprising when the structural formulæ of arginine and histidine are compared in proper relation; the former is a guanidine-aminopropionic acid, the latter an iminazole-aminopropionic acid; but on putting the formulæ side by side, we can see how closely they are related:



Histidine.



Arginine.

The essential molecular changes involved in passing from one to the other—the opening or closing of a ring and the addition or removal of an amino-group—we may, from our general knowledge of the chemical powers of the body, look on as essentially "physiological" processes. The strong suggestion which such preliminary nutritional experiments convey, that this or that reaction occurs in the body, should be followed by chemical studies. A final appeal to the animal can then be made. We want to know next how precisely on chemical lines histidine can be converted into arginine, and how the reverse change can be brought about. We could then test the ability of the animal, or of its various organs, to guide the reactions through the necessary intermediate stages. To say the truth, the nutritional fact is, in my belief, a sufficient proof that the reactions do occur, but a chemical study is required to help us to discover on what lines they may occur, as a guide for further experiments on the animal. From the animal to the laboratory and from the laboratory back to the animal is the logical order in such researches. The pure chemical studies should gain in interest, and certainly do not lose in dignity, from the fact that they deal with processes with which living tissues are concerned.

I return, before closing, to two further aspects of my subject, which can again be illustrated by experiments with free amino-acids. We have seen that different fractions of the protein molecule have different nutritional values. The question arises: Can the animal be maintained when supplied with only a limited number of amino-acids? Can it, for example, survive if, instead of protein or all the amino-acids contained in protein, it receives

only the more complex types of the latter, those which experiment shows to be outside the range of its synthetic powers. The question is doubtless somewhat academic, but it is of theoretical importance, and has one quite interesting bearing. If nutrition were possible on a quite limited number of amino-acids, we should be so much the nearer to the possibility of artificially synthesising our food supply; distant, in any practical sense, as that possibility may be. My own experiments have as yet given no conclusive answer to the question; but I have found that when an animal is fed on food containing only tryptophan, histidine, tyrosine, lysine, and cystine, that is, five out of the eighteen amino-acids of protein, there is a remarkably slow loss of weight, and long maintenance of apparent health. This result is in sharp contrast to what is seen when the five amino-acids mentioned are replaced by another five of simpler aliphatic type. When leucine, valine, alanine, and glycine, together with glutamic acid, form the sole nitrogen supply, loss of weight is rapid, and the animal soon succumbs. I feel it quite possible that further experiment will show that life can be maintained on a mixture from which many of the amino-acids of protein are lacking.

I now come to the last consideration with which I shall trouble you. In picturing the animal as it maintains itself on a supply of diverse amino-acids, we are entitled to ask, What are the various uses to which that supply is put? If the animal be a growing one, it must, of course, use a part for the construction of new tissue proteins; if an adult, for the repair of tissues. This involves a selective condensation of the various units into polypeptide complexes possessing a definite and specific stamp of structure. We have been already considering, in connexion with the weight curves which I have put before you, to what degree this or that deficiency in the supply can interfere with the progress of such synthesis. A second fate suffered by the amino-acids is immediate oxidation. It is very unlikely that the supply of them from the food will ever display the exact quantitative balance among the diverse units which will correspond with what is found in the specific tissue proteins of a given animal. During the selective regrouping, some individual acids will be in excess, and will be directly broken down on oxidative lines. In any case, protein as a whole is usually eaten in excess of the immediate needs, so that such direct oxidation is always going on. Our newer point of view as to the metabolic fate of protein lends greater interest to the study of these oxidations, because we are now aware that we have to follow the separate fate of individual amino-acids, which in each case is circumstanced by the properties of known

molecular structure. My desire to impress you with the immediate applicability of pure chemical considerations to the study of animal metabolism might, indeed, have been better served had I spent my time in reminding you of the knowledge which has been already won in connexion with these oxidations. There is much yet to learn about them, but patience and a good deal of real ingenuity has given us a mass of trustworthy information in what is, for the experimentalist, a very difficult domain. This ground has, however, been made familiar by the publication of certain excellent summaries, and I have preferred to deal with somewhat different aspects of the subject.

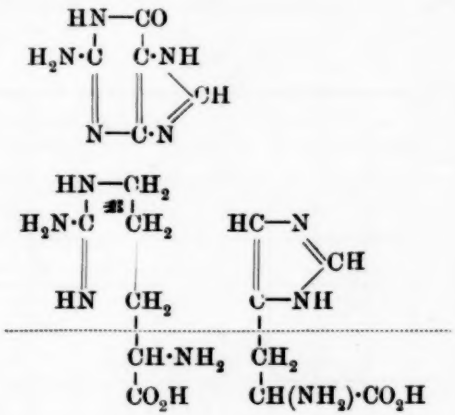
There is yet a third kind of use to which the body puts part of its amino-acid supply. Some of the units contribute directly or indirectly to the formation or upkeep of nitrogenous tissue complexes in which we do not find the structure of polypeptides or amino-acids. Other units probably undergo transformation into the specific constituents of secretions which possess a dynamic function. We have as yet scarcely any experimental information as to what particular (if any particular) amino-acid or acids may be the raw material satisfying this or that demand of the kind mentioned. We are consequently ignorant as to the nature of the reactions involved. We know that nitrogenous constituents of the living tissues, which are not themselves of a protein nature, can be made and maintained when only protein is eaten. Amino-acids, therefore, must be the ultimate raw material for such formations; but we do not know at what sort of level synthesis begins. It may be in this or that case that the body has chemical magic enough to be somewhat indifferent to the precise nature of the raw material, but some of the facts which have been already before you indicate that such indifference is not its habit.

At any rate, when some structural relationship is evident between a food-constituent and a tissue-constituent it is justifiable to suspect that the former, and not some wholly unrelated substance, provides the raw material for the manufacture of the latter. Such considerations at least provide a guide for experiment. In this connexion I want to call your attention to one other set of feeding experiments which bear on what I have just been saying.

Forming an integral part of the living cell nucleus are the polynucleotides or nucleic acids. These contain as essential units in their structure the purine bases adenine and guanine, which the growing animal can synthesise—as abundant experiment has shown—when eating no other nitrogenous material than protein.

Now the fact that the histidine molecule contains the iminazole

ring has suggested to others that it might play some special part in the formation of purines in the body, but the matter has not, in my opinion, been tested under conditions which could yield proper evidence. It may be remarked that arginine, like histidine, has one aspect of structure which is not found in any other amino-acid from protein, the presence, namely, of a carbon atom interposed between two nitrogen atoms. This is, of course, characteristic of the purine ring. It is perhaps worth while to compare the structure of arginine and histidine with that of one of the purine bases.



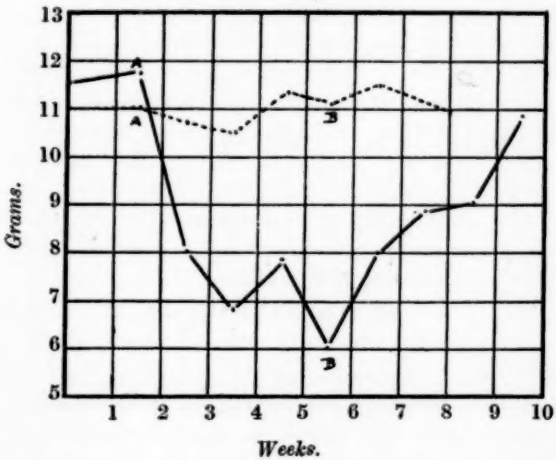
It would seem on inspection as though both these amino-acids might in some way share in the formation of the purine ring, but if, as I have claimed, the body can convert either one of them into the other, the point has small significance. It is in any case useless to speculate as to precise molecular relations in advance of chemical study; but the probabilities which exist fully justified a preliminary nutritional study, and I think I have obtained evidence on the matter which is highly suggestive, if not conclusive.

Purine metabolism in all animals, except man himself, ends with the excretion, not of uric acid as in man, but of allantoin, and if we are to determine whether any factor has influenced purine metabolism, we must estimate the allantoin of the urine. In the experiments to be referred to, the animals were first fed with a complete amino-acid mixture; then for a period arginine and histidine were withdrawn, while in the third period they were restored to the food. The urine was accumulated, and the allantoin estimated in the excretion of successive weeks. The lower curve in Fig. 6 shows the effect of the presence or absence respectively of arginine and histidine on the allantoin excretion.

There is a very marked fall as a result of their withdrawal, whilst their restoration is followed by a rise.

Such a result seems clearly to indicate a special relation between these particular amino-acids and the end-product of purine metabolism. It therefore suggests that they play a special part in the formation of the purine ring, but this conclusion must not be accepted without proper experimental controls. I must not stop to discuss the point fully or critically, but I can give you the evidence which removes the only important criticism. It might be justly argued that the fall in allantoin is due merely to the general depression of metabolism, due to the removal of a factor

FIG. 6.



The continuous line shows the effect of presence or absence of arginine and histidine on the excretion of allantoin. These two amino-acids were removed at A *and restored at* B. *Dotted line shows effect of removing and restoring tryptophan.*

essential to nutrition. We know already that there is a notable fall in weight when the animal receives no arginine or histidine. I have tried, however, the effect of other deficiencies which produce an equal or greater disturbance of nutrition on the excretion of allantoin. The upper curve in the figure shows the effect of removing tryptophan: this, as we know, involves complete failure of nutrition and a sharp fall in weight; but, as you will see, there is no similar effect on the excretion of allantoin. I have tried the result of other deficiencies, also with negative results. There can be little doubt that arginine and histidine play a special part in purine metabolism, but here again the full proof requires the

assistance of the organic chemist. We want next to trace the intermediate stages of the reactions which intervene in the conversion of the amino-acid into a new type of structure. I would like, indeed, to feel that the few facts and the more numerous suggestions which have been before you this evening—facts and suggestions won in a very narrow field of research—may suffice to leave behind the impression in your mind that, because intermediary metabolism deals so largely with materials of which the actual molecular structure is known or ascertainable, the trained thought of the organic chemist has abundant opportunities in connexion with physiological research. We have dealt with protein metabolism alone, but it is equally true of metabolism in all its aspects. You may urge, of course, that the formation of the tissue complexes with their extreme chemical elusiveness is, after all, the most significant step in metabolism; so in a sense it is. The physical and physico-chemical properties of these complexes confer on the living cell its prominent mechano-motor properties and many of its reactivities, as well as providing the milieu in which chemical reactions occur. In my own belief, however, these complexes, once formed, are, in the chemical sense, essentially stable in all but one particular. Just as they are formed and maintained by the condensation (in the technical sense of the word) of the simpler molecules which are ever circulating in the blood, so are they liable to hydrolytic disintegration, yielding, like the food, simple materials for fresh synthesis or materials to undergo oxidation and provide energy to the body. Condensation and hydrolysis respectively lock and unlock the door which prevents or permits the occurrence of those oxidations and that regrouping of units which form the essential chapter in the chemical dynamics of metabolism. On the other side of that door there is relative chemical stability. About the details of condensation and hydrolysis in the tissues we have an indefinite amount to learn, but in connexion with large aspects of metabolism they may be taken for granted. If we follow our molecules of known structure up to the door, and follow them yet again as they emerge from it, we shall learn a large part of what we want to know about the chemical dynamics of the animal body.